THE PRODUCTION OF CARBON BLACK BY THE THERMAL DECOMPOSITION OF ACETYLENE AND ACETYLENE-HYDROCARBON MIXTURES

Approved:

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Dean of the Graduate School

THE PRODUCTION OF CARBON BLACK BY THE THERMAL DECOMPOSITION OF ACETYLENE AND ACETYLENE-HYDROCARBON MIXTURES

DISSERTATION

Presented to the Faculty of the Graduate School of
The University of Texas in Partial Fulfillment
of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY

by

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PREFACE

Recognition and appreciation are gratefully acknowledged to Dr. E. P. Schoch, Director of the Bureau of Industrial Chemistry, for his direction of this project. His encouragement and new ideas, at times when each attempt to move forward had met with failure, were the incentive which led to whatever success this work might claim. Unreserved thanks are expressed to the writer's co-worker, Mr. Jack Burks, for his many contributions to this project and for his untiring work.

Each member of the Bureau of Industrial Chemistry has contributed in some way to this project. The writer expresses his thanks to Drs. K. I. Glass, H. A. Holcomb, W. B. Howard, A. S. Kasperik, G. E. Montes, W. L. Ray, Max Samfield; Messrs. A. M. Cuellar, R. P. Lightfoot, J. W. Sheehan, J. L. Weeks, Miss Colleen Moore; and shop personnel W. L. Benson, J. L. McGee, P. K. Pruett, and J. W. Roper.

Thanks are also due Mr. Bruce Blount and Mr. R. H. Ellis-Anwyl, Research Assistants of the Research Laboratory in Ceramics, for advice and help in the manufacture of refractories and to the Humble Oil and Refining Company for the mass spectrograph analysis of gas samples.

October, 1947

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INTRODUCTION

A process for the manufacture of acetylene by means of an electric discharge through hydrocarbon gases has been developed by the Bureau of Industrial Chemistry at the University of Texas. Several projects to find new industrial uses for acetylene have been carried on by the Bureau of Industrial Chemistry in parallel with the acetylene process development, one of which, the thermal decomposition of acetylene into carbon black, is discussed in this report. Acetylene has been decomposed into carbon black on a commercial basis for a number of years by the Shawinigan Chemicals Limited of Canada, but all details of the process have been held in secret. The work here, consequently, was started with the knowledge that the process was workable, but with no knowledge of how the reaction was effected. The aim of this project is to develop the know-how of the acetylene decomposition reaction in order to facilitate the widest usage of acetylene.

The relatively high cost of acetylene manufactured from calcium carbide has, in the past, restricted the use of carbon black from acetylene. The lower cost of acetylene manufactured by electric discharge processes, however, reduces the cost of acetylene black so that it can compete with carbon black made by other processes. Acetylene black

is widely used where high thermal and electrical conductivity is desired, but its demand is small in fields where cheaper carbon blacks can be used. The acetylene black made by the process described in this report is now being evaluated to determine its adaptability to the major fields of carbon black usage.

SUMMARY

When acetylene is heated above 800° C. it decomposes into carbon black and hydrogen. The reaction proceeds quietly and the yield of carbon black is in excess of 97 per cent of theoretical with optimum operating conditions and apparatus dimensions. The acetylene throughput can be varied from 10 to 30 pounds per hour without affecting the per cent of acetylene decomposed, and throughput of 50 pounds per hour is likely to give the same high yield. The product gas from the process is essentially pure hydrogen, i. e., 99 per cent hydrogen. The reaction is highly exothermic, and some of the liberated heat can be utilized to crack other hydrocarbon gases. A gas mixture of 30 per cent natural gas, 70 per cent acetylene can be decomposed to give a yield of 90 per cent of the total carbon therein, while a 20 to 80 mixture of propane and acetylene gives a similar yield. Lesser proportions of the acetylene diluent give correspondingly higher yields of carbon black. Dilutions of less than (1) 13 per cent natural gas and (2) 9 per cent propane give yields of 99 per cent, indicating the diluent is completely decomposed. Mixtures of hydrogen and acetylene up to a mixture containing 59 per cent hydrogen produce 97 per cent of their carbon content as carbon black.

The apparatus consists of a, so called, run "burner"

which serves to introduce the gases into the decomposition chamber, a refractory to form a retaining wall for the reacting gases, and auxiliary equipment to remove carbon black from the product gas. The design of this run burner and the diameter of the refractory involve the items which determine both the workability of the process and the yield of carbon. The run burner is designed to keep the acetylene cool until it is released within the refractory, to deliver the acetylene at an optimum velocity, and to flush hydrogen constantly across the end ~~of~~ or "face" of the burner to prevent the formation of coke upon that surface.

All evidence indicates that the decomposition of acetylene proceeds by a chain mechanism which is propagated by chain carriers of atomic hydrogen and stopped by collision with the wall. It is the effect of the wall upon the chain reaction which makes the refractory diameter a critical factor in the apparatus design. Refractories larger than 9½ inches allow the reaction to proceed essentially to completion while smaller refractories give decreasingly smaller yields.

The decomposition apparatus has been operated for periods of slightly more than one hour, but for continuous operation it needs only the addition of equipment for the continuous removal of carbon black.

THE ACETYLENE DECOMPOSITION PROCESS

The process represented by the equation

$$C_2H_2(g) = 2C(s) + H_2(g)$$

has a standard free energy at 25° C. of

$$\Delta F° = -50.0 \text{ kcal./g.mol.}$$ [1]

Hence acetylene has a great tendency at 25° C. to decompose into its elements. The decomposition at this temperature is so slow, however, that it is undetectable. If the temperature of the acetylene is raised slowly, polymerization sets in at 400°C. or at even lower temperatures in the presence of certain metals or other contact catalysts,[2] while decomposition becomes noticeable at approximately 500° C. and becomes the chief reaction at 800° C.[3] The decomposition of acetylene is essentially complete above 1000° C.

Catalysts have been found to promote the decomposition of acetylene, but these catalysts, in general, have proven unsatisfactory for continuous acetylene decomposition. The

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[1] Pitzer, to be published; Perry, John H., Editor, Chemical Engineer's Handbook, McGraw-Hill Book Company, New York, 2nd Ed., p. 550.

[2] Nieuwland, Julius A., The Chemistry of Acetylene, Reinhold Publishing Corporation, New York, 1945, p. 138.

[3] Ibid., p. 15.

catalysts either become coated with carbon and lose their effectiveness or are eroded by acetylide formation. While the acetylide decomposes to form carbon and to regenerate the metal catalyst, yet the regenerated catalyst is entrained within the carbon and is unavailable for further use.

The decomposition of acetylene at 1000° C. is a highly exothermic reaction.

$$\Delta H^{\circ}_{1000\,^{\circ}C.} = -53.5 \text{ kcal./g.mol.}$$ [4]

It is possible, therefore, to have a flow process with the reaction proceeding spontaneously if the heat given off by the decomposing acetylene can be passed to the incoming acetylene.

Let Q = energy required to heat one g. mol. of acetylene from 18° to 1000° C.

C_p = average specific heat over this temperature range.

Then, $Q = \Delta T \cdot C_{p(C_2H_2)}$

$= (1000 - 18)(15.8)$

$= 15.5$ kcal./g.mol.

A glance at the ratio, $\Delta H_{1000\,^{\circ}C.}/Q$, shows that over three times more heat is produced by the reaction than is necessary to heat an equal amount of feed acetylene to the reaction

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[4] See Appendix I for calculation of ΔH° at 1000°C.

temperature. In a flow process, however, the products of the reaction tend to carry away from the reaction zone most of the heat liberated by the reaction. The feed gas can receive heat by radiation from the decomposition products and from a refractory lining in the reaction zone or the decomposition reaction can proceed by a chain mechanism. The latter means of energy transmission seems more likely and is discussed in a later section.

It is necessary for the acetylene molecule to have a rapid energy input in order to carry it rapidly through the polymerization stage and into the decomposition stage. Too slow an energy input will, of course, allow polymerization of the acetylene to take place in preference to decomposition. The rapid heating of acetylene to its decomposition temperature in unpacked tubes gives a sudden decomposition[5] with no appreciable polymerization. The use of packed tubes or small diameter reaction vessels retards or completely stops the reaction.

The flowsheet for the thermal decomposition of acetylene is very simple. Acetylene is fed through a burner into a refractory which has been previously heated to approximately 1000° C. The acetylene decomposes inside the refractory with the formation of hydrogen and carbon black. The product

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[5] Nieuwland, op. cit., p. 141.

gas is led through a carbon separator where much of the carbon is knocked out and the gas is then filtered to remove the remaining "fines." The product gas is essentially hydrogen--the main impurities being those which enter with the acetylene. The process flowsheet is given in Figure 1.

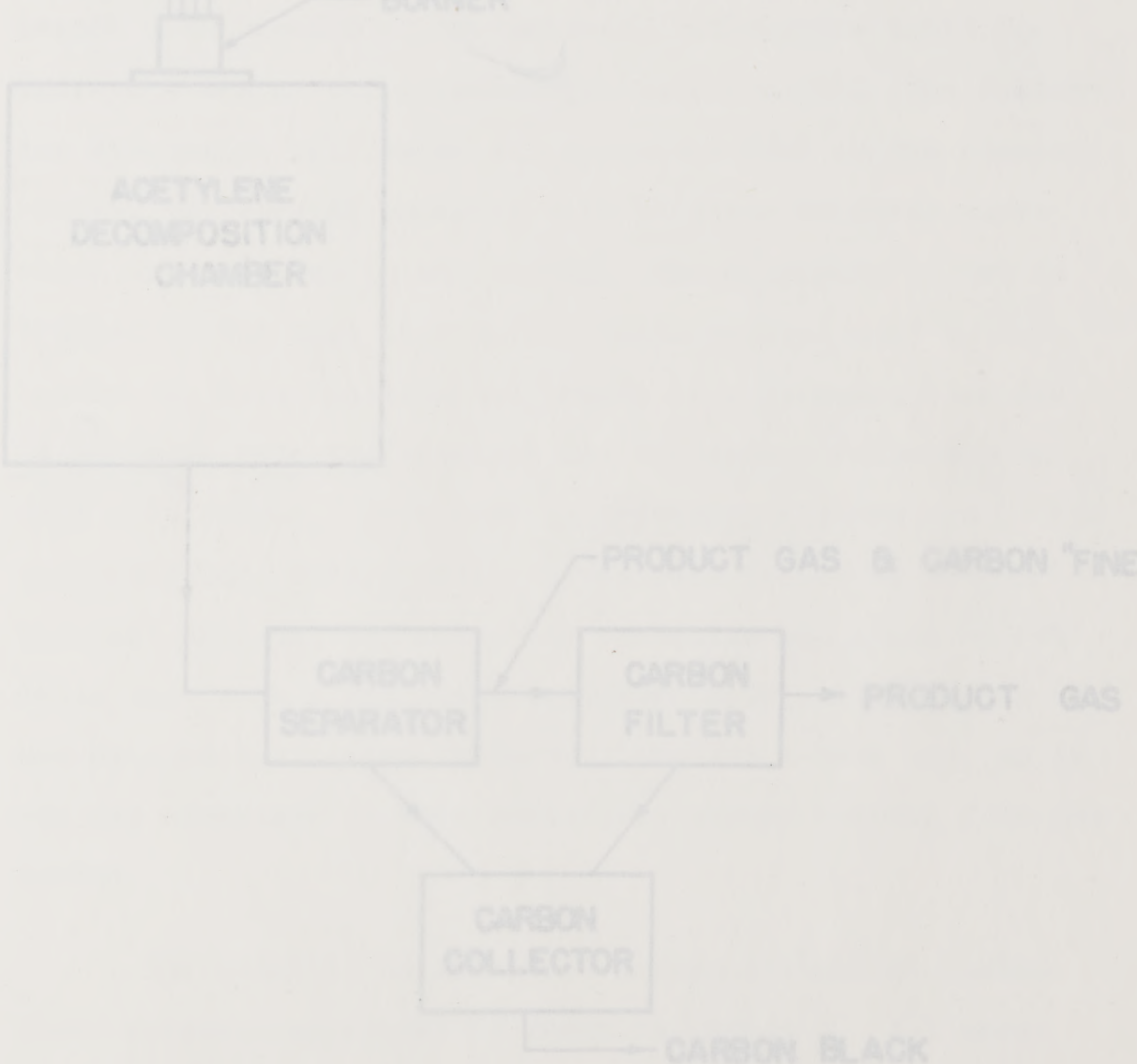


FIG. 1. PROCESS FLOWSHEET.

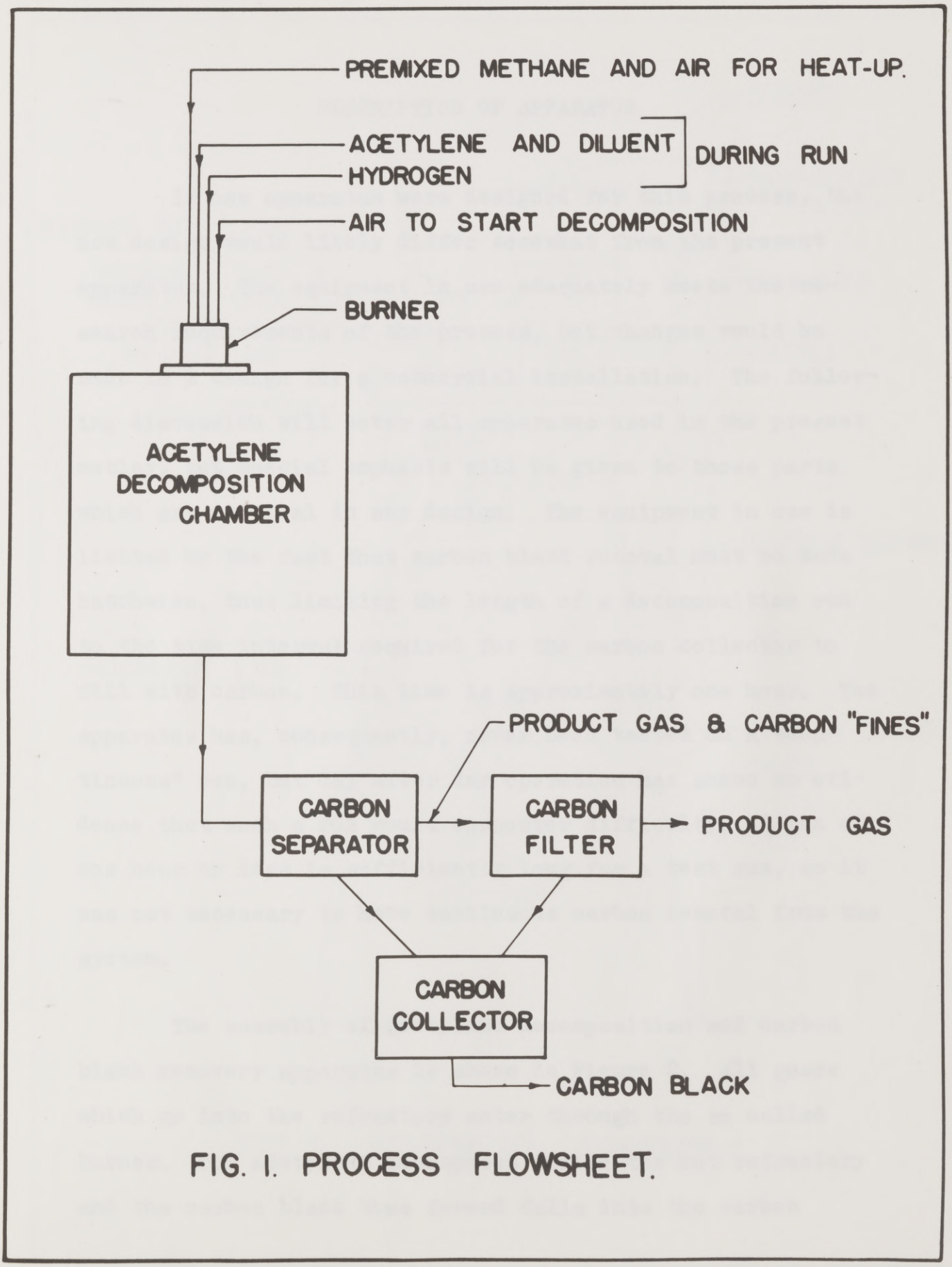


FIG. 1. PROCESS FLOWSHEET.

DESCRIPTION OF APPARATUS

If new apparatus were designed for this process, the new design would likely differ somewhat from the present apparatus. The equipment in use adequately meets the research requirements of the process, but changes would be made in a design for a commercial installation. The following discussion will cover all apparatus used in the present outlay, but special emphasis will be given to those parts which are critical in any design. The equipment in use is limited by the fact that carbon black removal must be made batchwise, thus limiting the length of a decomposition run to the time interval required for the carbon collector to fill with carbon. This time is approximately one hour. The apparatus has, consequently, never been tested on a "continuous" run, but day after day operation has shown no evidence that such a run would encounter difficulty. A run of one hour or less is sufficiently long for a test run, so it was not necessary to have continuous carbon removal from the system.

The assembly of acetylene decomposition and carbon black recovery apparatus is shown in Figure 2. All gases which go into the refractory enter through the so called burner. The acetylene decomposes inside the hot refractory and the carbon black thus formed falls into the carbon

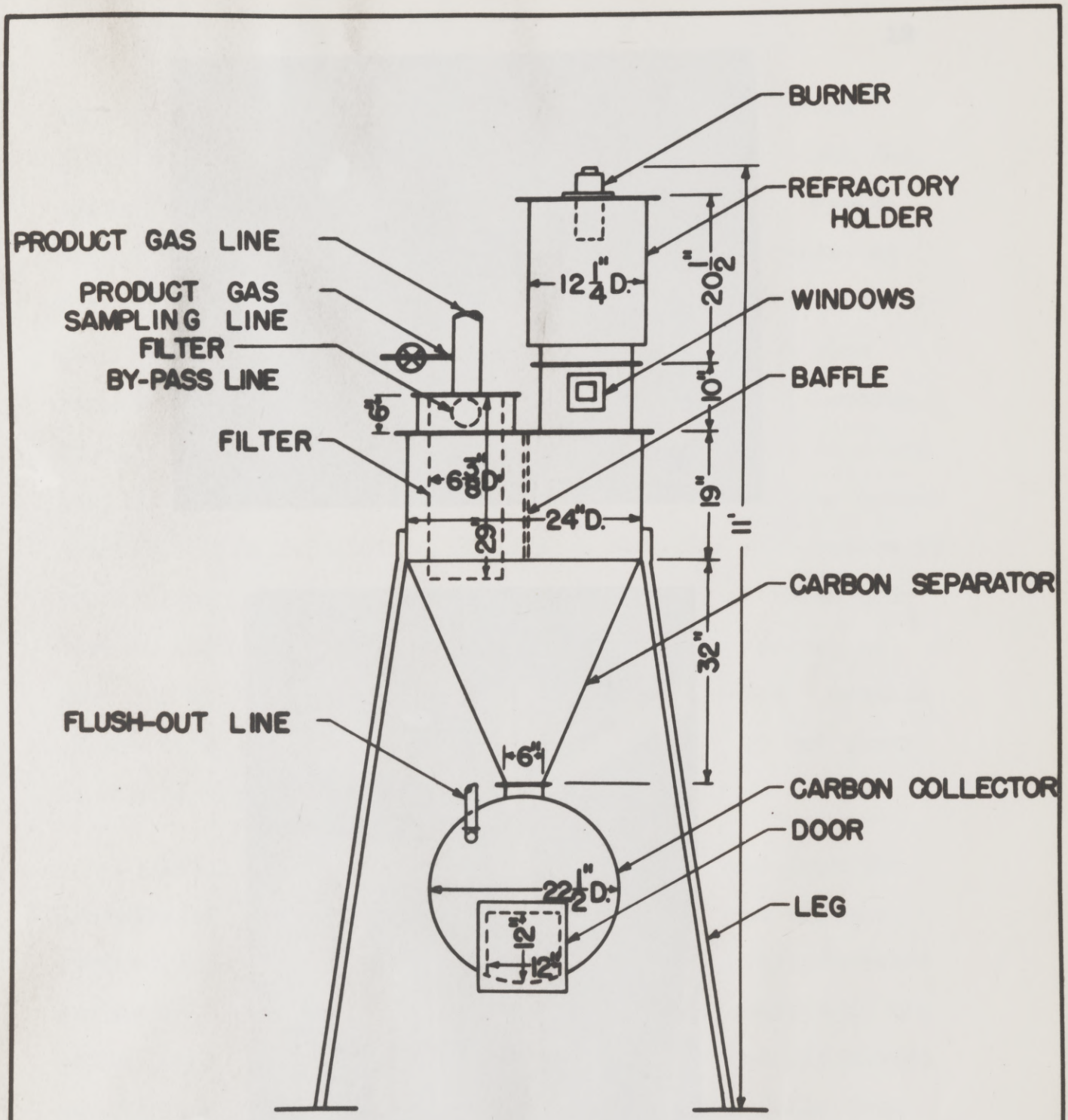
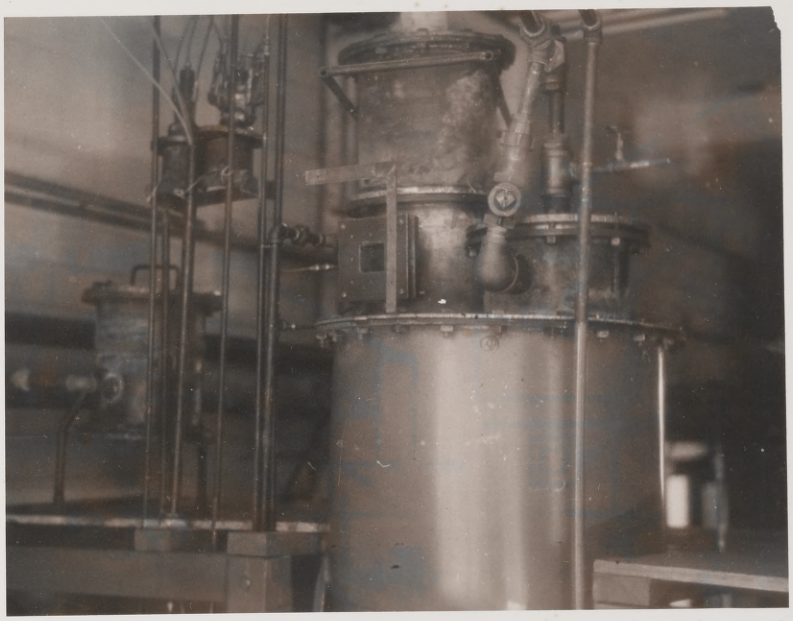


FIG. 2. EQUIPMENT ASSEMBLY.



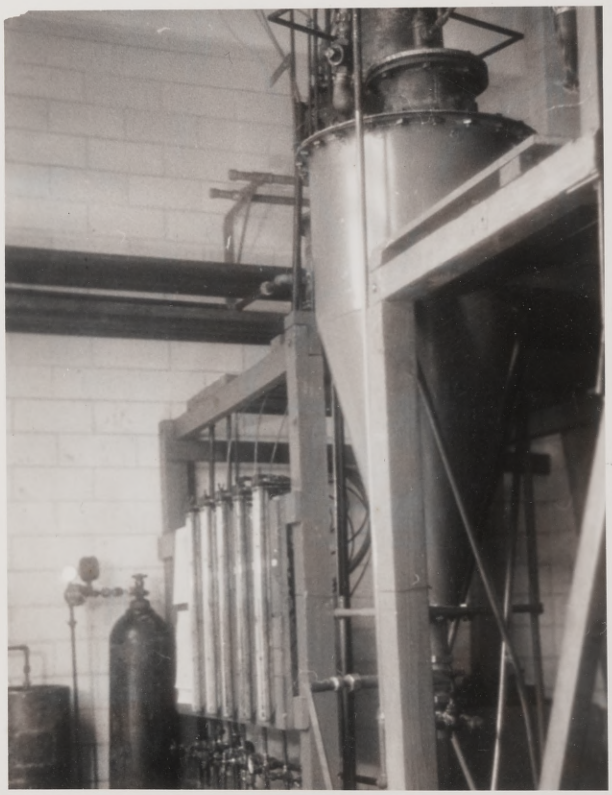


FIGURE 2a. Acetylene Thermal Decomposition Apparatus

separator. The section of 10 inch diameter pipe placed directly beneath the refractory and forming a duct from the refractory to the carbon separator is equipped with Pyrex plate glass windows, which are placed on opposite sides of the pipe and are used to observe when decomposition is occurring. A light placed in front of one window can be seen through the other only when no carbon is falling in between. Excellent decomposition is shown when carbon heated to a red heat can be seen falling from the refractory; mediocre decomposition shows no color in the carbon but only the absence of transmitted light. Natural gas is blown against these windows to keep them free of carbon black and, of course, is shut off when a sample of the product gas is taken. Details of the window design are discussed in Appendix II and shown in Figure 16.

Much of the carbon flocculates as it comes from the decomposition chamber and the floccules fall from the gas product stream into the carbon collector. The unflocculated carbon is carried by the gas stream around the baffle in the carbon separator and to the filter. The filtered gas passes out through the product gas line and the carbon falls from the filter into the collector.

The structural parts of the apparatus are made of low carbon steel. The gas is cooled only by natural heat losses

from the apparatus unless it is desired to meter the product gas. It is essential that these heat losses be allowed to take place and not be hindered by insulation since the gas temperature is sufficiently high to melt the steel.

The refractory is heated prior to a decomposition run using the "heat-up" burner shown in Figure 3. Any method of heating the refractory is satisfactory,but for convenience, the heating is done by burning a premixed stream of natural gas and air inside the refractory. This heat-up burner is similar to an ordinary laboratory gas-air burner except (1) all air enters as primary air and (2) the end of the burner is water cooled. The air used during heat-up is controlled so that a neutral or reducing atmosphere is maintained within the apparatus. When the refractory has attained the decomposition temperature, this burner is removed and replaced with the run burner which supplies the acetylene. The run burner is shown in Figure 4. Its sole purpose is to introduce acetylene into the hot refractory, but the difficulty of that job is indicated by the complexity of the design. Its development was tedious and its design involves the most essential features of the process. These features will now be discussed.

It is desirable to keep the acetylene as cool as possible until it is released from the run burner into the

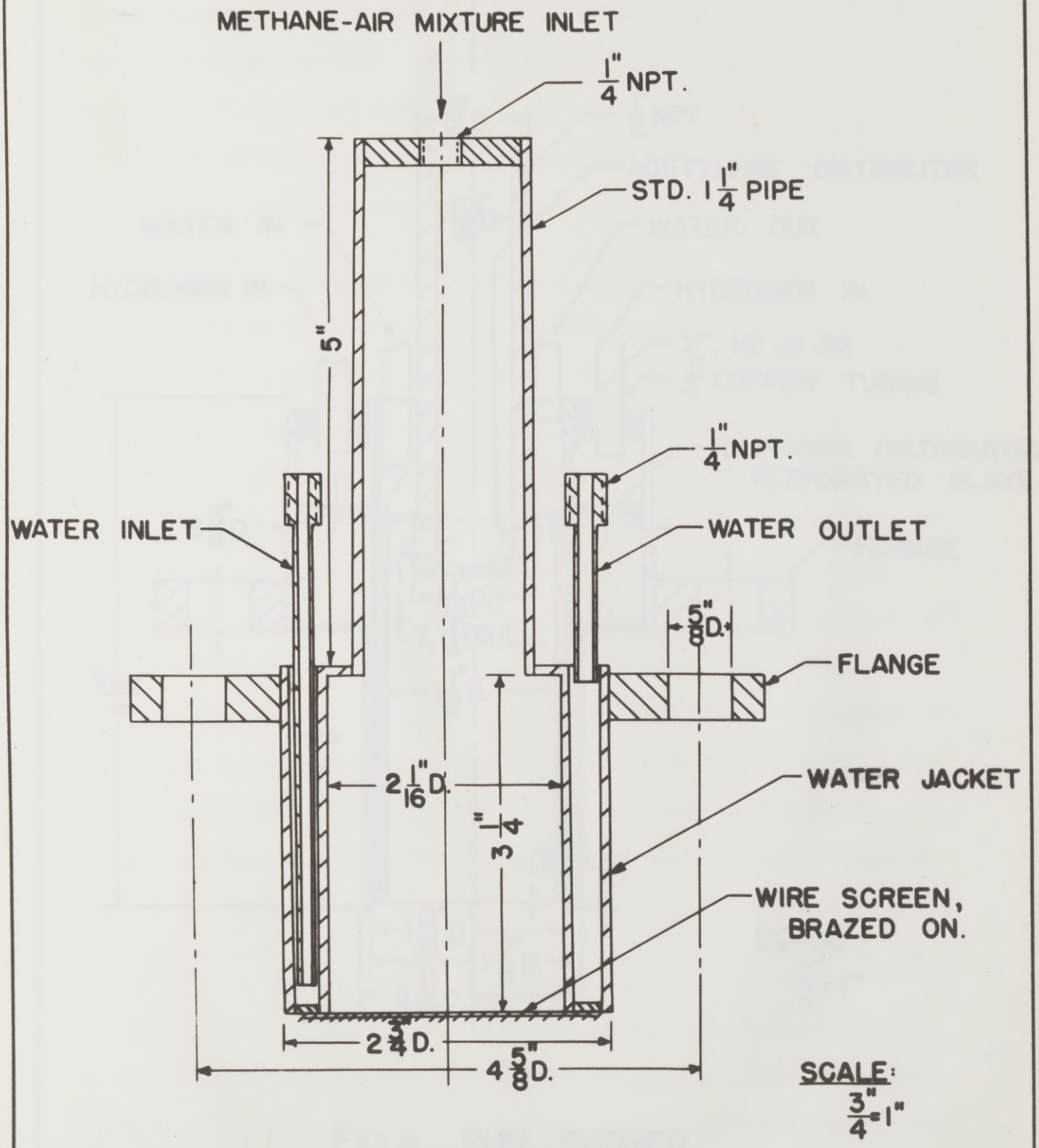


FIG. 3. HEAT-UP BURNER.

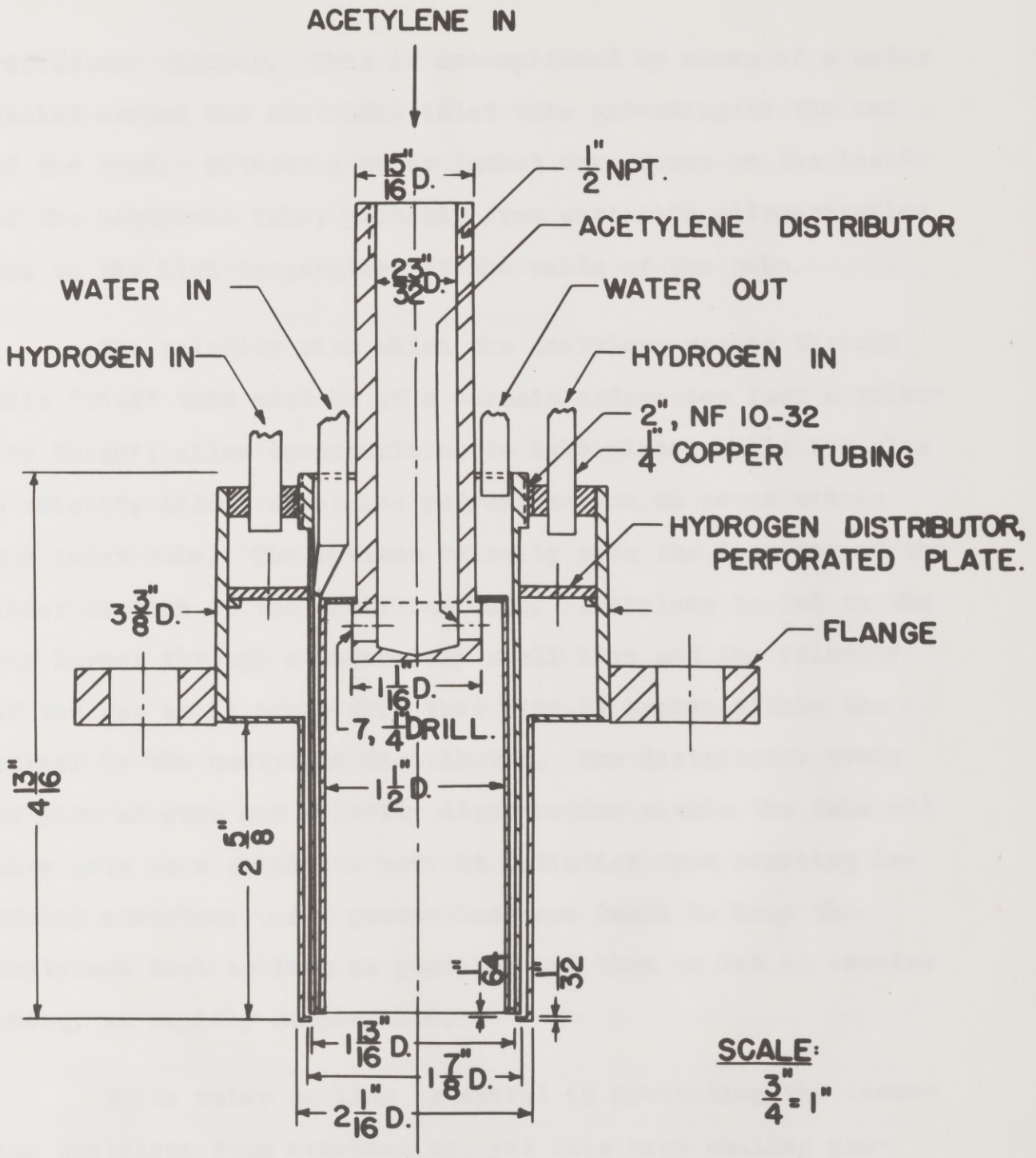


FIG. 4. RUN BURNER.

refractory chamber. This is accomplished by means of a water jacket around the acetylene inlet tube extending to the end of the tube. Without a water jacket coke forms on the inside of the acetylene tube, probably from excessive polymerization due to the high temperature of the walls of the tube.

The velocity with which the acetylene passes through this "feed" tube must be of a certain order--too fast a velocity doesn't allow decomposition to take place, while too slow a velocity allows excessive polymerization to occur within the inlet tube. The optimum velocity sets the diameter of the lower section of the acetylene tube. Acetylene is fed to the run burner through a moderately small line and the velocity of the gas as it comes from this line is broken within the burner by the acetylene distributor. The distributor tends to give an even gas velocity distribution within the tube and also acts as a shield to prevent radiation from reaching incoming acetylene. All precautions are taken to keep the acetylene cool as long as possible and then to let it receive energy as rapidly as possible.

While water cooling is useful in protecting the incoming acetylene from overheating, yet this very cooling produced trouble in another manner. Although no coke will form on the water-cooled "inside" walls of the acetylene tube, yet coke will quickly form on the so called "face" of the water

jacket, i. e., that part of the water jacket at the bottom of the burner and extending at right angles to the major axis of the burner. The coke which starts on the face of the water jacket will grow until it nearly extends across the end of the acetylene tube. When such a condition is reached, decomposition will no longer continue.

This formation of coke on the burner was eliminated by two changes: (1) the thickness of the water jacket was reduced to a minimum and (2) an inert gas was blown across the face of the water jacket to prevent any acetylene from reaching this spot. The path for cooling water inside the water jacket is 1/16 inch wide--so narrow that circulating water must be forced to the bottom of the jacket and not merely introduced with a tube. The face of the water jacket is 3/16 inches wide and hydrogen blows continuously across its surface to prevent any acetylene from contacting the face. The hydrogen enters the burner in an annular space around the water jacket and its inlet velocity to this space is broken by a distributor. The tube forming the annular space around the water jacket has a very thin lip at the lower end which directs the stream of hydrogen across the water jacket face.

When in use, this run "burner" is bolted to the top of the refractory holder. It extends through the ceiling of the refractory and releases the acetylene one inch below this

ceiling. The position of the burner in relation to the refractory is shown in Figure 5. The distance the run burner extends into the refractory is another critical factor. It should be very nearly one inch--with only a slight deviation therefrom. If the burner face is placed flush with the refractory ceiling, coke will form on this refractory surface adjacent to the burner and soon bridge across the burner with the result that the acetylene decomposition is stopped. Several trials have shown that the acetylene will not decompose when the burner face is lowered until it is approximately three inches below the refractory ceiling.[6] A distance of one inch from the refractory to the burner face has given very satisfactory results.

The refractory now in use is made of alundum and was purchased from the Norton Company. It has satisfactorily withstood rapid temperature changes and has not spalled. It is obvious that in a commercial installation a refractory could not be tolerated which would spall so much as to spoil the carbon black.

The chemical composition of the refractory has no effect upon the decomposition, but its physical dimensions, --i. e., diameter and shape--do affect the acetylene decomposition. Both of the above factors are discussed in

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[6] These trials were made with a refractory which was 10 3/8 inches long, which shows, incidentally, that a longer refractory will possibly support the decomposition.

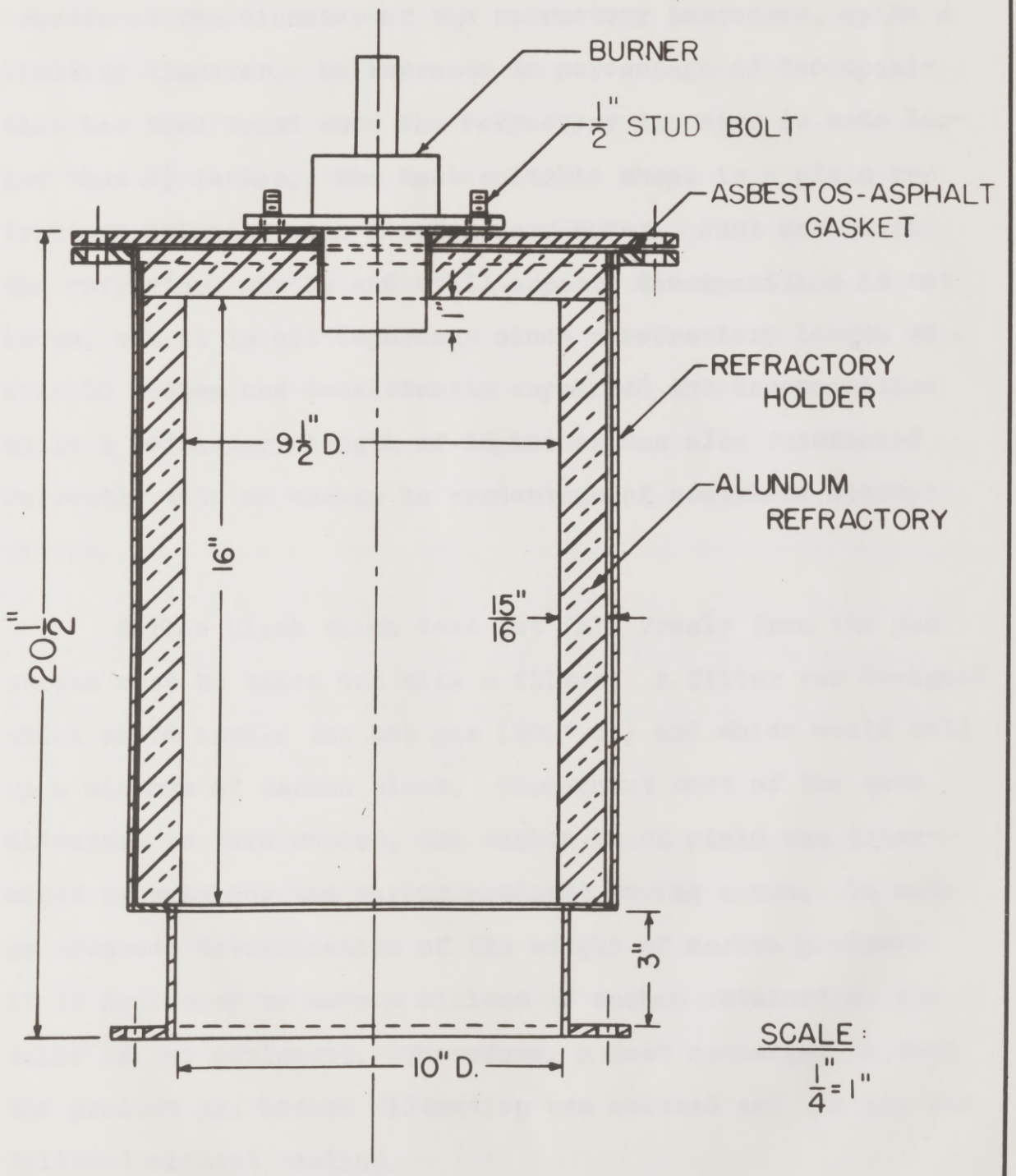


FIG. 5. BURNER-REFRACTORY ASSEMBLY

following sections. The per cent of acetylene decomposed increases as the diameter of the refractory increases, up to a limiting diameter. No increase in percentage of decomposition has been found when the refractory diameter is made larger than 9½ inches. The most suitable shape is a plain refractory cylinder with a refractory cover. Just how short the refractory can be and still support decomposition is not known, but it is not important since a refractory length of only 10 inches has consistently supported the decomposition while a refractory length of 16 inches has also functioned correctly with no change in percentage of acetylene decomposition.

Carbon black which does not fall freely from the gas stream must be taken out with a filter. A filter was designed which would handle the hot gas (400° C.) and which would hold up a minimum of carbon black. Throughout most of the work discussed in this report, the carbon black yield was determined by weighing the carbon produced during a run. To make an accurate determination of the weight of carbon produced it is necessary to have a minimum of carbon retained on the walls of the equipment. Therefore, a heat exchanger to cool the product gas before filtration was omitted and the gas was filtered without cooling.

Fiberglas cloth has been found to be a suitable filter

medium which will both remove the finely divided carbon black and withstand the high temperature of the gas. The carbon black filter is shown in Figure 6 and consists of a cylindrical support wrapped with glass cloth. The support is a section of 6-inch diameter pipe sealed at one end and fitted with a smaller pipe at the other end for removal of the filtered gas. The 6-inch pipe is perforated with numerous 5/8-inch diameter holes to allow passage of the gas into the pipe. The 6-inch pipe is first wrapped with copper window screening and then wrapped with Fiberglas cloth on top of the screening. Both the screening and the cloth are tightly bound with wire to hold them to the pipe. The purpose of the screening is (1) to form a continuous support for the cloth, extending over the holes in the cylinder and (2) allow gas filtration to take place over the entire area of the cloth and not just over the holes in the cylinder.

Carbon black adheres to the glass cloth and forms a constantly growing layer. Much of the carbon falls off, but the layer continues to grow. The cloth cannot be flexed to remove the carbon black since it becomes brittle at elevated temperatures and it cannot be scraped since anything more than gentle contact will cause the cloth to tear. During the experimental work the filter was removed after each series of two or three runs and cleaned with a vacuum cleaner. Only a

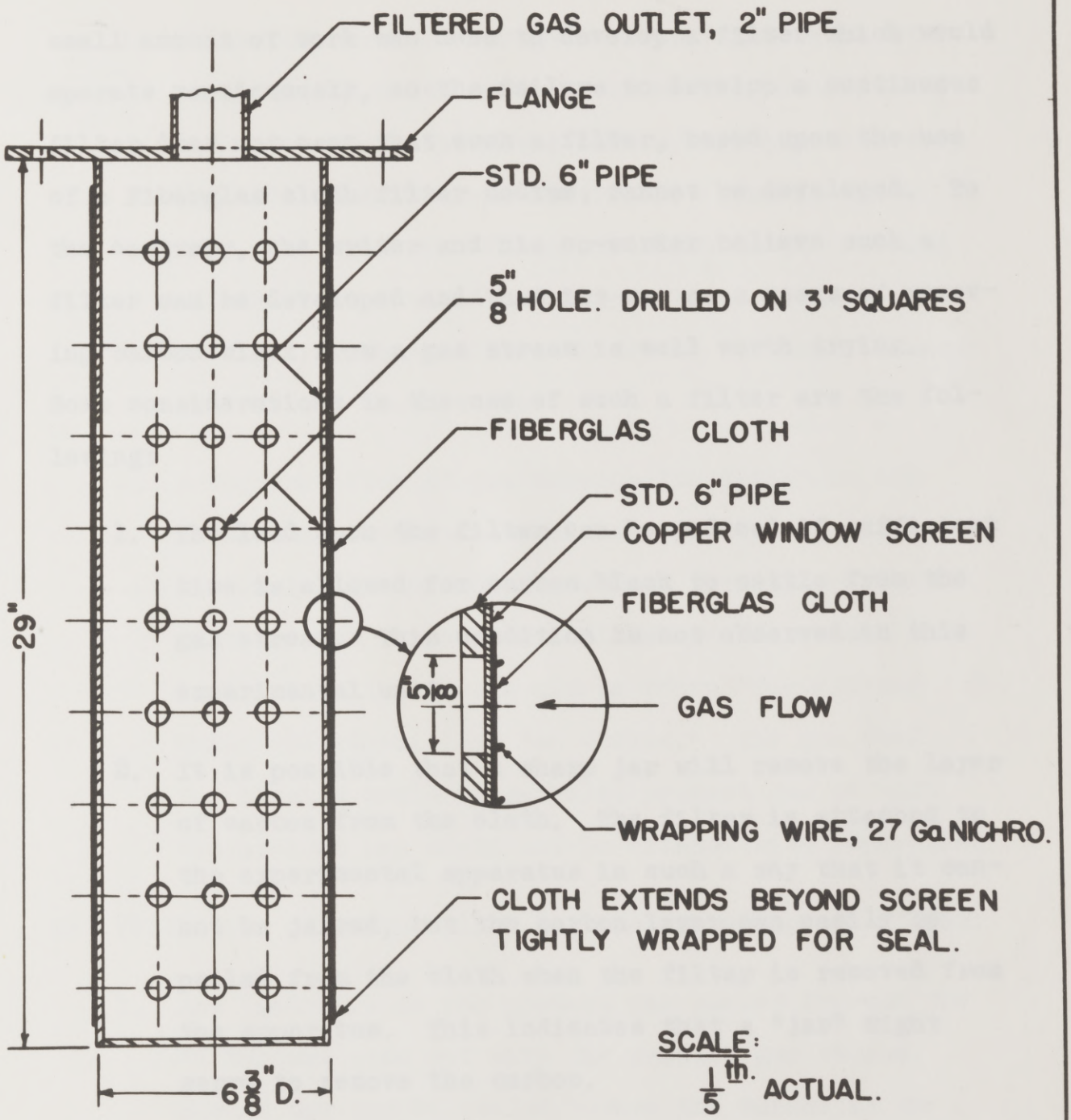


FIG. 6. CARBON BLACK FILTER.

small amount of work was done to develop a filter which would operate continuously, so the failure to develop a continuous filter does not mean that such a filter, based upon the use of a Fiberglas cloth filter medium, cannot be developed. To the contrary, the writer and his co-worker believe such a filter can be developed and that its use as a means of removing carbon black from a gas stream is well worth trying. Some considerations in the use of such a filter are the following:

1. The load upon the filter can be reduced if sufficient time is allowed for carbon black to settle from the gas stream. This condition is not observed in this experimental unit.

2. It is possible that a sharp jar will remove the layer of carbon from the cloth. The filter is attached to the experimental apparatus in such a way that it cannot be jarred, but the carbon layer can easily be peeled from the cloth when the filter is removed from the apparatus. This indicates that a "jar" might serve to remove the carbon.

3. Possibly a scraper can be devised which will withstand the high temperature and will not injure the cloth when it scrapes off the carbon. Wrapping an additional layer of wire screening over the cloth

allows the use of a rough metal scraper since it protects the cloth, but the screening becomes plugged with carbon and gives such a high pressure drop that its usefulness is destroyed. Brushes which will not injure the Fiberglas cloth as they scrape off the carbon would probably have to be made of a material which would not withstand the high temperature of the product gas.

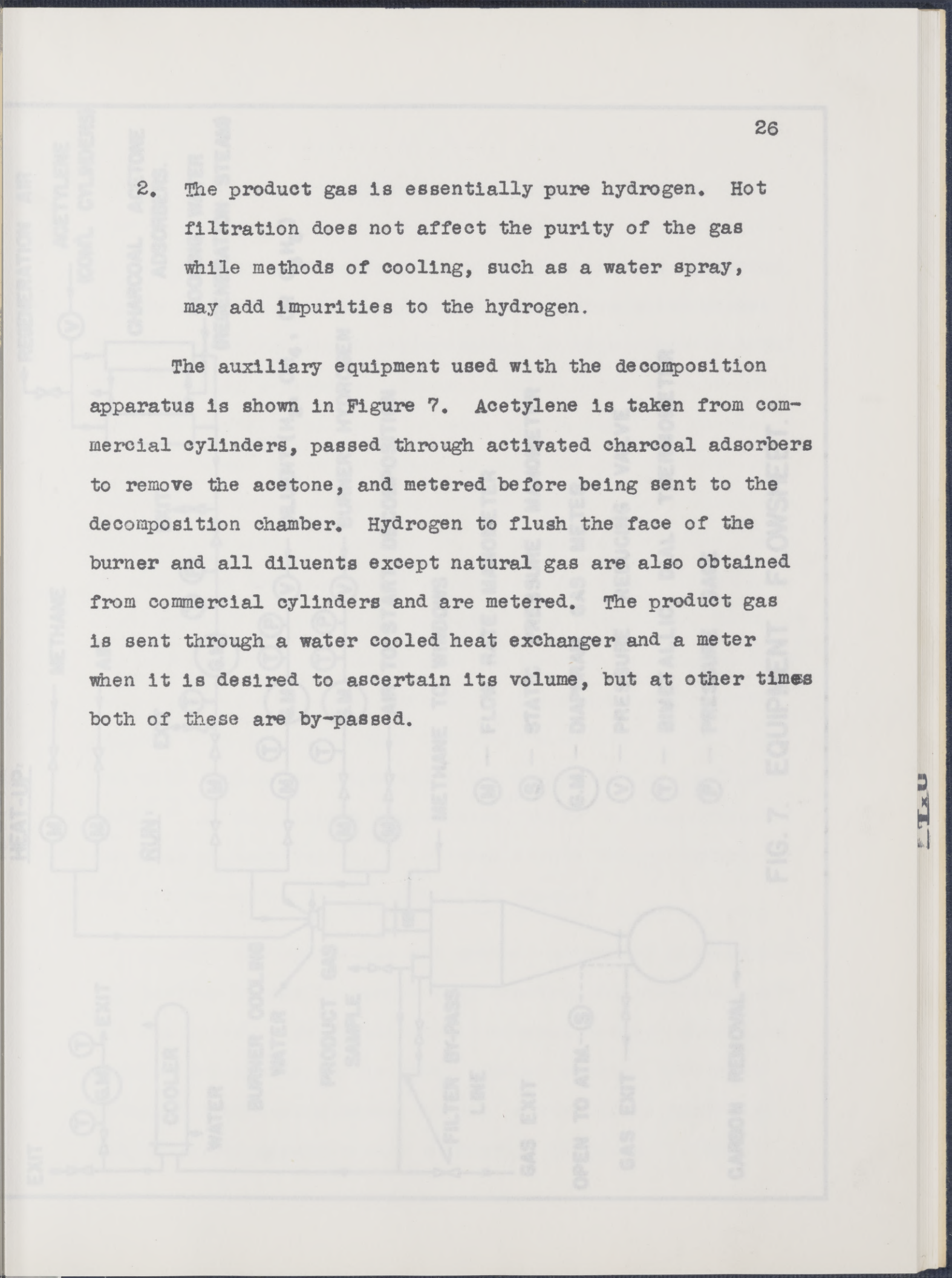
4. A vigorous flow of gas through the filter in the reverse direction seems to have good possibilities of blowing the carbon layer from the filter cloth. In this case two or more filters would be used in parallel so that one could be "down" for blowing while the other(s) is "on stream." The gas used for blowing would be recycled product gas so that the product gas would not be diluted with impurities.

Hot filtration of carbon black has the following advantages:

1. Any "polymer" in the product gas passes through the filter and goes out with the product gas stream. Should the gas be cooled before the carbon is removed, any high boiling compound in the gas will condense upon the carbon. An appreciable amount of condensed "polymer" adversely affects the properties of the carbon black.

2. The product gas is essentially pure hydrogen. Hot filtration does not affect the purity of the gas while methods of cooling, such as a water spray, may add impurities to the hydrogen.

The auxiliary equipment used with the decomposition apparatus is shown in Figure 7. Acetylene is taken from commercial cylinders, passed through activated charcoal adsorbers to remove the acetone, and metered before being sent to the decomposition chamber. Hydrogen to flush the face of the burner and all diluents except natural gas are also obtained from commercial cylinders and are metered. The product gas is sent through a water cooled heat exchanger and a meter when it is desired to ascertain its volume, but at other times both of these are by-passed.



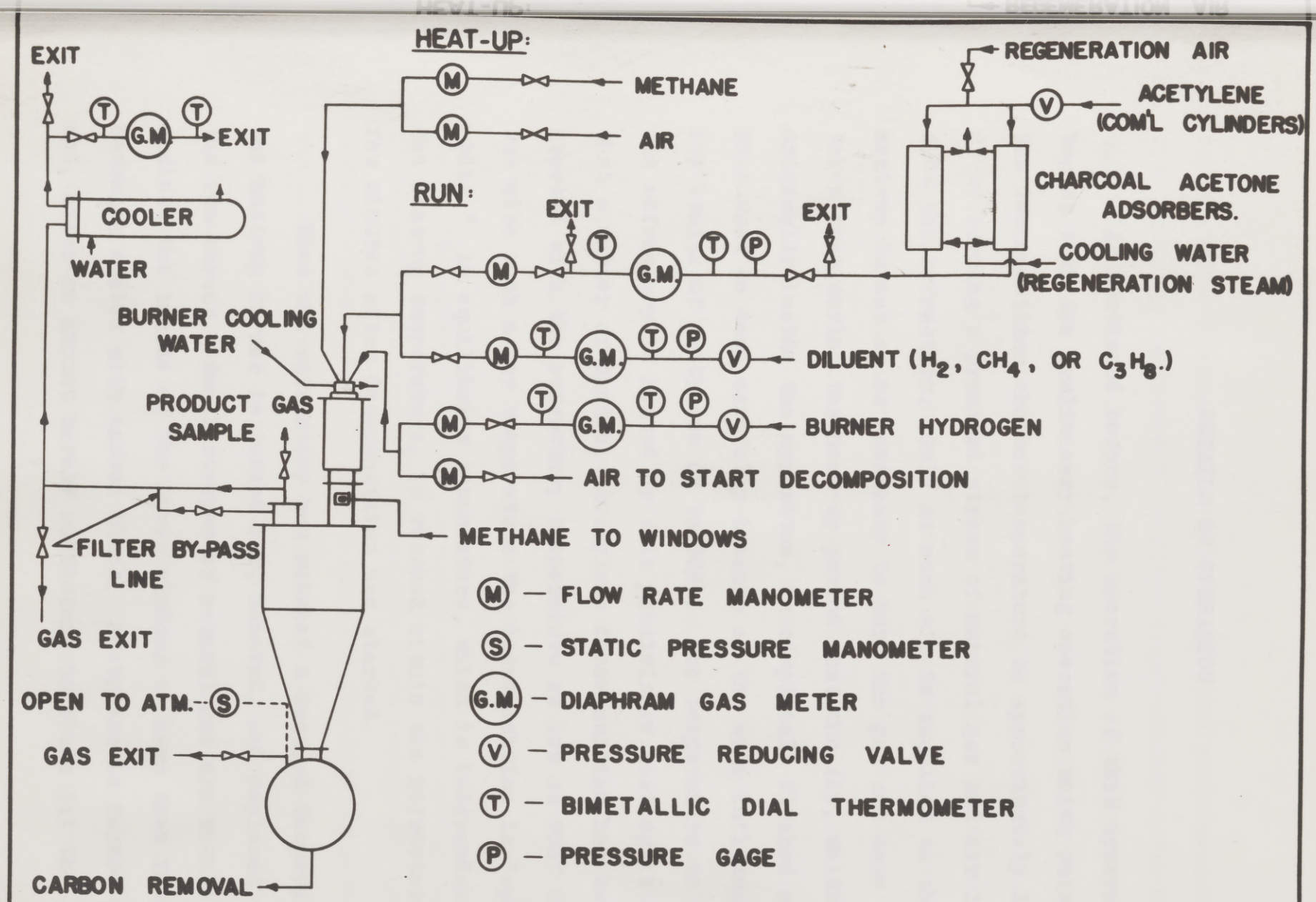


FIG. 7. EQUIPMENT FLOWSHEET.

DETAILS OF OPERATION

As mentioned before, the operation of this apparatus begins with the preliminary heating operation which raises the decomposition chamber temperature to approximately 1000° C. by burning a premixed stream of natural gas and air inside the refractory. Only as much air is supplied to the heat-up burner as is necessary to burn the gas and care is taken that during the heat-up period that the air, which was originally inside the apparatus, is completely flushed out. This must be done carefully because of the wide inflammability limits of acetylene (2 to 85%). The temperature to which the refractory is heated by this preliminary heating is somewhat a matter of choice. Acetylene decomposition has been started with the refractory temperature as low as 600° C., but with such a low temperature the decomposition is "spasmodic." An equilibrium temperature, which is independent of the heat-up temperature, is reached within the refractory a few minutes after decomposition has started.

When the refractory has reached a desired temperature, the heat-up burner is turned off, removed, and replaced with the run burner. Small streams of natural gas are then blown against the inside of the Pyrex windows to keep them from becoming coated with carbon black. Acetylene is turned on and, after an amount barely sufficient to flush out the

refractory has entered, a small stream of air is turned on. The resulting explosion starts the decomposition. Thus the explosion occurs with only a small amount of acetylene in the system and, consequently, isn't violent enough to be dangerous. When the preliminary heating has raised the refractory temperature to a "near orange" color the acetylene will occasionally start to decompose before air is added, but usually the above mentioned explosion is needed to start the decomposition. The air-acetylene mixture is ignited by contact with the hot refractory in refractories of 10 inches diameter and smaller, but in larger refractories a pilot burner is used. The pilot burner is employed only to ignite the air-acetylene mixture and is turned off after decomposition starts. It takes so long for an inflammable mixture of air and acetylene to reach the wall in large refractories that the explosion is too vigorous to be safe.

The addition of air is continued approximately one minute after the explosion to ensure continuation of the decomposition. The air may be shut off immediately after the explosion, but the decomposition proceeds more smoothly if the addition of the air is continued until all irregularities in the gas flow caused by the explosion have passed. Hydrogen is fed to the run burner as soon as the addition of air is stopped, and its flow is continued throughout the run. Both air and hydrogen, respectively, are fed

to the burner through the same annular space surrounding the water jacket so that each, in turn, prevent acetylene from touching the face of the water jacket and this avoids coke formation.

Decomposition proceeds smoothly and quietly when the operating conditions are suitable. The apparatus needs very little attention during a run; the maintenance of a steady gas input is the only requirement. This attention can be eliminated if the acetylene and hydrogen sources are kept under constant pressure and if pressure rise within the apparatus is avoided. It is essential that the apparatus be operated under positive pressure to prevent leakage of air into the system since both acetylene and its gaseous decomposition product, hydrogen, are highly explosive. Back pressure from the filter and the exit line automatically gives a positive pressure to the system. A decomposition run is stopped simply by shutting off the feed gases. The system is then flushed out with natural gas, allowed to cool, flushed out with air, and the carbon black removed.

A run is always started with pure acetylene. If a run is to be made on a mixture of acetylene and some diluent, the diluent is not fed into the acetylene stream until the decomposition of the pure acetylene is proceeding smoothly. The diluent is fed into the acetylene line some distance

upstream from the burner so that the acetylene and the diluent are thoroughly mixed before the gas enters the decomposition chamber. The rate of diluent input is increased slowly so as to avoid a sudden change in gas composition. The decomposition reaction in this chamber is much like that in the engine of a car, which may choke and even stop when the accelerator is stepped on too rapidly. It often takes as long as five minutes to increase the percentage of diluent methane in the feed gas from zero to 30 per cent. A sudden rate change of either the acetylene or of the diluent will often cause the decomposition to cease.

After the desired gas rates are set and the reaction is proceeding smoothly, the stream of methane directed on the windows is cut off so that it won't contaminate the product gas samples. The rates of all inlet gases and the product gas are then taken simultaneously by means of diaphragm type gas meters. The gas pressure at the meter and the gas temperature both before and after the meter are recorded. It is often found that the gas temperature will change during passage through the meter. A choke connected to a differential manometer is also placed in each inlet gas line so that the rate can be kept essentially constant at some set value.

Immediately after the gas rates have been determined, a sample of the product gas is taken for analysis. The gas

rates are then changed and another set of readings recorded or the run is stopped as desired.

RESULTS

I. Decomposition of Acetylene

Acetylene when heated may undergo many different reactions--only one of which is its decomposition into carbon black and hydrogen. The degree of decomposition of the acetylene is affected by both the physical dimensions of the decomposition chamber and by the feed rate of the acetylene. Both factors have been tested and rated in terms of yield of carbon black. The yield of the decomposition reaction is calculated as the percentage of acetylene which decomposes into carbon black.

A. Variation of Yield with the Dimensions of the Refractory.

The breakdown of acetylene into carbon and hydrogen is greatly influenced by the diameter of the decomposition chamber. The fraction of acetylene which decomposes increases with increase in diameter of the refractory until a yield of approximately 98 per cent is reached. The smallest refractory which gives this high yield has a $9\frac{1}{2}$ inch diameter, while the largest refractory tested has a diameter of $12\frac{1}{2}$ inches and it too gives a high yield. These results are shown graphically in the lower curve of Figure 8.

Carbon clings to the wall of the refractory and builds up until the gas volume diameter, i. e., the diameter of the

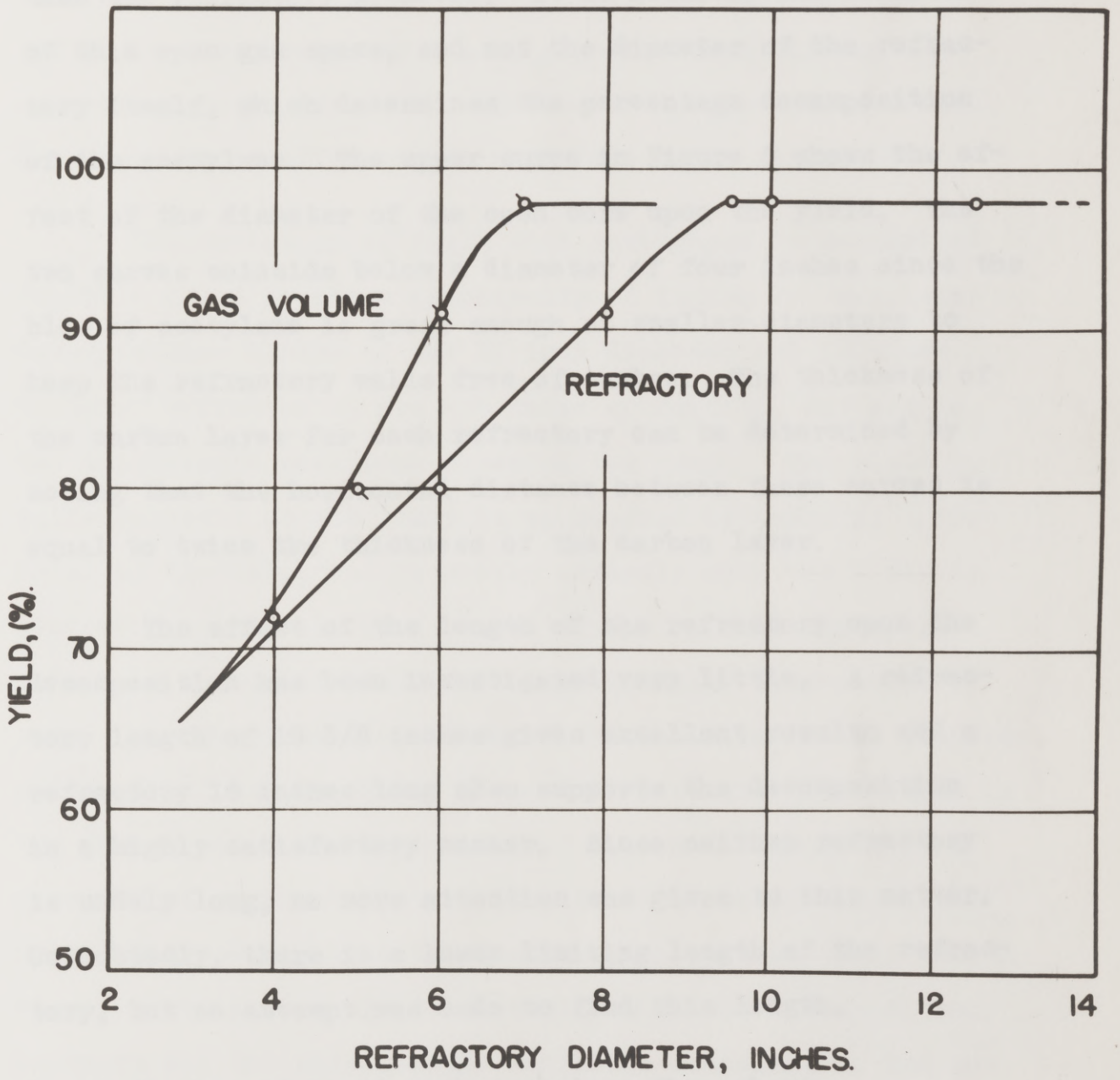


FIG. 8. VARIATION OF YIELD WITH REFRACTORY DIAMETER.

open core through the center of the carbon, is much smaller than the refractory diameter. It is actually the diameter of this open gas space, and not the diameter of the refractory itself, which determines the percentage decomposition of the acetylene. The upper curve in Figure 8 shows the effect of the diameter of the open core upon the yield. The two curves coincide below a diameter of four inches since the blow of acetylene is great enough at smaller diameters to keep the refractory walls free of carbon. The thickness of the carbon layer for each refractory can be determined by noting that the horizontal distance between these curves is equal to twice the thickness of the carbon layer.

The effect of the length of the refractory upon the decomposition has been investigated very little. A refractory length of 10 3/8 inches gives excellent results and a refractory 16 inches long also supports the decomposition in a highly satisfactory manner. Since neither refractory is unduly long, no more attention was given to this matter. Undoubtedly, there is a lower limiting length of the refractory, but no attempt was made to find this length.

B. Variation of Yield with Acetylene Throughput.

There is a lower limit of acetylene input for each refractory diameter and as the latter is increased, this limit is raised. An upper input limit has not been reached

with any refractory although attempts have been made to find such a limit. At high acetylene rates the load upon the gas filter is very heavy and causes a prohibitive rise in the apparatus static pressure. The use of larger carbon removal equipment would allow higher acetylene input rates.

The variation of yield with throughput is summarized in Table I and is shown graphically in Figure 9. The lower decomposition limits of the 10-inch diameter and 12½-inch diameter refractories are not known accurately, but are in the approximate positions shown on the graph. The yield remains constant as the limit is approached by means of a lowering of the rate, and it breaks suddenly when the limit is reached. At this limit a slight change in throughput can produce a change of yield from approximately 98 per cent to zero. The decomposition, however, is unstable in the vicinity of the limit and is easily stopped by a slight fluctuation in the throughput. The decomposition apparatus should not be operated at an input close to the limit since decomposition which stops so easily often starts again spontaneously with a vigorous explosion. In other words, when the decomposition restarts all the sufficiently undiluted acetylene in the apparatus decomposes. Such explosions should be carefully avoided.

The extrapolated section of the curve in Figure 9 is

TABLE I

VARIATION OF YIELD WITH THROUGHPUT OF ACETYLENE

Run No.	Gas Sple.	Refractory Diameter	Acetylene Rate $ft^3/hr.$ STP	Acetylene Rate lb./hr.	Yield (%)	Comments
Y-6	-	10"	116	7.4	96	Average acetylene rate over the entire run. Yield calculated from the weight of carbon produced.
Y-4	-	"	123	8.4	95	
Y-5	-	"	137	9.4	98	
YN-4	JJ-75	"	189	12.9	97.8	All following runs have instantaneous rates. The yield is calculated from inlet and product gas analyses.
YN-5	JJ-86	"	254	17.4	97.5	
YN-4	JJ-74	"	264	18.1	97.1	
YN-6	JJ-97	"	307	21.0	97.6	
YN-7	JJ-114	"	407	27.8	97.5	
YN-7	JJ-114	"	419	28.6	97.5	
NN-2	JJ-81	9½"	247	16.9	97.3	
NN-3	JJ-84	"	277	19.0	97.3	
NN-2	JJ-80	"	278	19.0	97.3	
NN-8	JJ-113	"	423	29.0	97.6	
NN-8	JJ-113	"	433	29.6	97.4	
NN-7	-	"	529	36.2	-	Decomposition was smooth but yield was not determined.
Z-7	-	12½"	205	14.0	-	Decomposition stopped when rate dropped to approximately this value.
ZN-2	JJ-94	"	245	16.8	98.6	
ZN-2	JJ-93	"	290	19.8	97.3	
ZN-3	JJ-100	"	320	21.9	97.3	
ZN-4	JJ-115	"	390	26.7	97.4	
ZN-4	JJ-115	"	419	28.6	97.4	

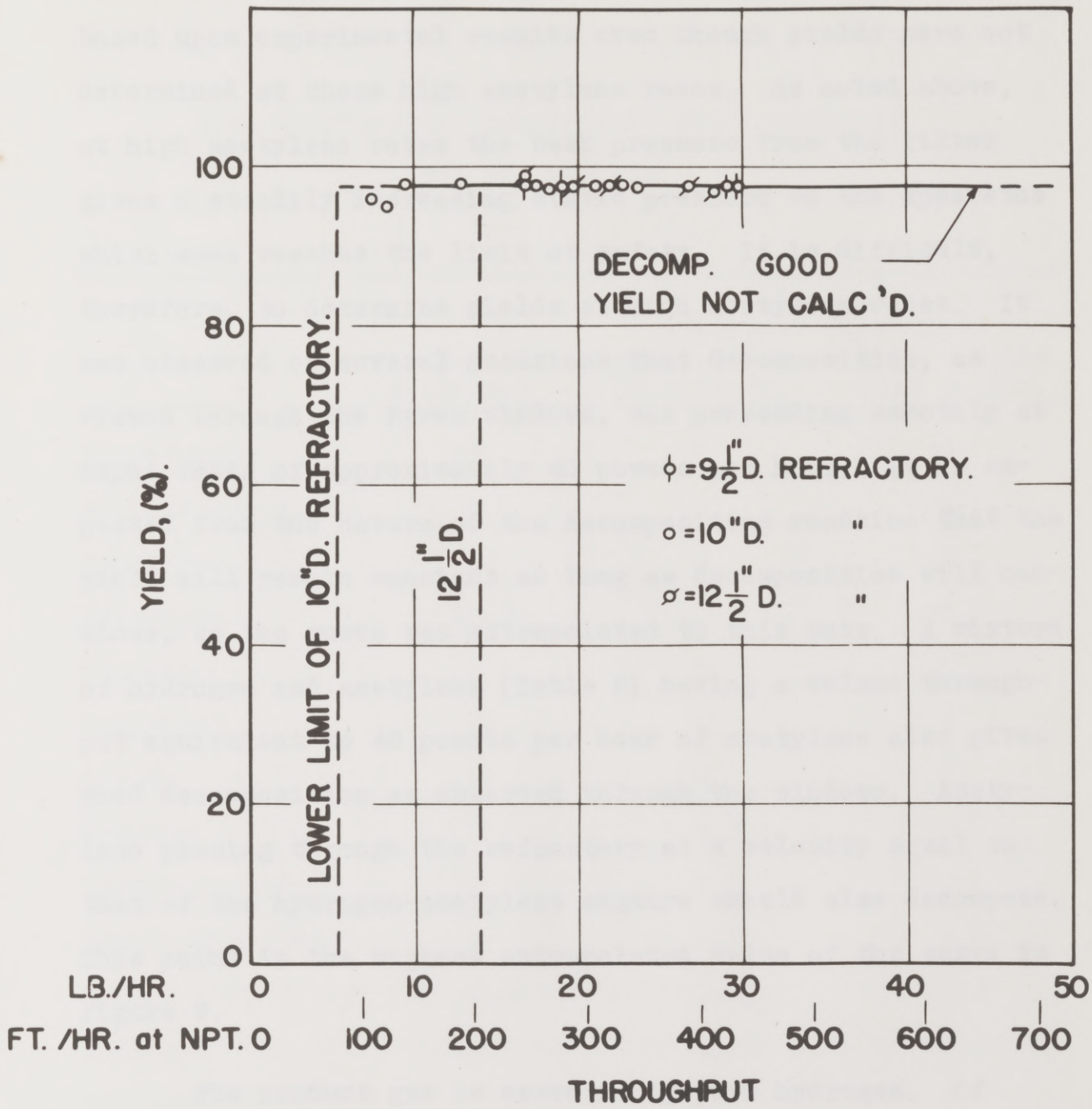


FIG. 9. VARIATION OF YIELD WITH THROUGHPUT.

based upon experimental results even though yields were not determined at these high acetylene rates. As noted above, at high acetylene rates the back pressure from the filter gives a steadily increasing static pressure on the apparatus which soon reaches the limit of safety. It is difficult, therefore, to determine yields at high acetylene rates. It was observed on several occasions that decomposition, as viewed through the Pyrex windows, was proceeding smoothly at input rates of approximately 40 pounds per hour. It is expected from the nature of the decomposition reaction that the yield will remain constant as long as decomposition will continue, so the curve was extrapolated to this rate. A mixture of hydrogen and acetylene (Table 5) having a volume throughput equivalent to 46 pounds per hour of acetylene also gives good decomposition as observed through the windows. Acetylene passing through the refractory at a velocity equal to that of the hydrogen-acetylene mixture should also decompose. This point is the highest extrapolated value of the curve in Figure 9.

The product gas is essentially pure hydrogen. Of course, impurities in the feed acetylene will affect the product gas and a fraction of one per cent of methane is formed from the thermal equilibrium between carbon and hydrogen. The mass spectrograph analyses of feed acetylene and product gas at two throughput rates are given in Table II. The carbon

TABLE II

MASS SPECTROGRAPH ANALYSES OF FEED ACETYLENE AND PRODUCT GAS

	Feed Acetylene	Product Gas Acetylene Input Rate Sple. JJ-84 19.0 lb./hr	Sple. JJ-104 26.6 lb./hr.
Diacetylene	ST	0	0
Methyle acetylene	0	0	0
Ethylene	0	0	ST
Acetylene	99.8	0	ST
Propane	0	0	0
Propylene	0	0	0
Ethane	0	0	0
Methane	0	0.3	0.3
Carbon Dioxide	0	0	0
Carbon Monoxide	0	0.2	0.2
Water	0.2	0.4	0.3
Hydrogen	ST	99.1	99.2
Oxygen	0	0	0
Nitrogen	0	0	0

T = Trace = 0.03 - 0.04%
ST = Slight trace = 0.01 - 0.02%

monoxide and the extra water which appear in the product gas are traces of flue gas from the heat-up period. The absence of higher acetylenes and the complete breakdown of the acetylene should be noted.

II. Decomposition of Acetylene--Diluent Mixtures

The highly exothermic nature of the acetylene decomposition reaction gives the possibility of cracking other compounds by utilizing part of the heat. The heat from the acetylene decomposition can obviously be best utilized by thoroughly mixing the gaseous compound to be cracked with the acetylene prior to decomposition. The extraneous gas has the role of a diluent during the decomposition and is referred to as such in this report. This distinction is made to differentiate between adding the extraneous gas to the acetylene prior to the reaction or mixing it with the product gas after the reaction has taken place.

A. Results of Acetylene-Diluent Decomposition

Two types of diluent were used in this work: (1) a hydrocarbon diluent which will increase the yield of carbon black through its own decomposition, and (2) an inert diluent which undergoes no reaction. Natural gas and propane were used as the hydrocarbon diluent--natural gas since its relative cheapness makes it a logical choice and propane because

of its high carbon content and ease of cracking. Hydrogen was tested as an inert diluent to determine how concentrated the acetylene must be before it will undergo satisfactory decomposition. If the acetylene is obtained from a process which produces acetylene by an electric discharge through hydrocarbon gases, the cost of concentrating the acetylene can be reduced if a sufficiently dilute acetylene-hydrogen feed gas will decompose. The acetylene as produced in the electric discharge is highly diluted with hydrogen.

Yields from diluent runs were (1) based on total available carbon in the feed gas, and (2) based on the theoretical carbon from the acetylene in the feed gas. The meaning of the first calculation is self evident and the second indicates the percentage of carbon contributed by the diluent. Results of diluent decomposition trials are given in Tables III to V and are shown graphically in Figure 10 and Figure 11. The upper limit of dilution with hydrogen is approximately 59 per cent hydrogen while the limit with natural gas is 30 per cent and 21 per cent for propane. The presence of hydrogen has no effect upon the decomposition of acetylene until the limit is exceeded and the decomposition is stopped. Natural gas is completely decomposed in dilutions under 13 per cent while higher dilutions show a slightly decreasing yield. Propane exhibits a similar curve with dilutions of 9 per cent and less undergoing complete dissociation.

TABLE III

VARIATION OF YIELD WITH NATURAL GAS DILUTION

(9½" d. Refractory)

Run No.	Gas Sple.	Acetylene Rate lb./hr.	Natural Gas Rate lb./hr.	Volume % Natural Gas	Yield (%) Based on C_2H_2	Yield (%) Based on Total Carbon
AMNN-1	JJ-116	21.3	0.97	6.8	102.3	98.3
"	JJ-117	21.0	1.37	9.4	105.6	99.8
"	JJ-118	21.7	1.69	11.0	106.7	99.8
"	JJ-119	20.7	1.94	13.0	108.1	99.7
AMNN-2	JJ-122	22.2	3.10	18.1	108.0	96.2
"	JJ-123	20.8	4.21	24.4	110.8	93.8
AMNN-4	-	17.7	4.70	29.8	-	-
	This mixture decomposed. A slight increase in natural gas rate, however, stopped the decomposition.					
AMNN-5	JJ-127	16.8	4.15	28.3	112.6	92.2
	Slight adjustment in acetylene rate after this reading was taken caused decomposition to stop.					

TABLE IV

VARIATION OF YIELD WITH PROPANE DILUTION

(9½" d. Refractory)

Run No.	Gas Sple.	Acetylene Rate lb./hr.	Propane Rate lb./hr.	Volume % Propane	Yield (%) Based on C_2H_2	Yield (%) Based on Total Carbon
APNN-1	JJ-129	19.9	2.03	4.8	104.9	97.9
"	JJ-130	19.6	2.50	6.0	108.5	99.5
"	JJ-131	19.0	3.54	8.5	112.8	99.6
"	JJ-132	16.9	4.20	11.0	115.3	98.1
APNN-2	JJ-134	17.9	5.76	13.7	114.7	93.5
"	JJ-135	16.7	7.19	17.4	- +	- +
"	JJ-136	17.3	8.75	20.0	122.1	90.1

A slight increase in propane rate stopped decomposition.

+ Gas sample bulb leaked giving an unreliable gas analysis.

TABLE V

VARIATION OF YIELD WITH HYDROGEN DILUTION

(9½" d. Refractory)

Run No.	Gas Sple.	Acetylene Rate lb./hr.	Hydrogen Rate lb./hr.	Volume % Hydrogen	Yield, (%)
NNH-1	JJ-87	21.2	0.34	16.4	- +
"	JJ-88	18.6	0.50	24.7	- +
"	JJ-89	16.8	0.56	28.8	97.8
NNH-2	JJ-91	17.7	0.83	36.4	97.8
NNH-3	JJ-107	16.2	1.15	46.5	96.8
NNH-4	JJ-137	18.1	1.15	43.7	98.2
"	-	18.0	1.44	49.4	- +
"	-	18.3	1.73	53.6	- +
"	-	18.8	2.17	58.5	- +
	A slight increase in the hydrogen rate stopped decomposition.				

+ Decomposition good. Yield not calculated.

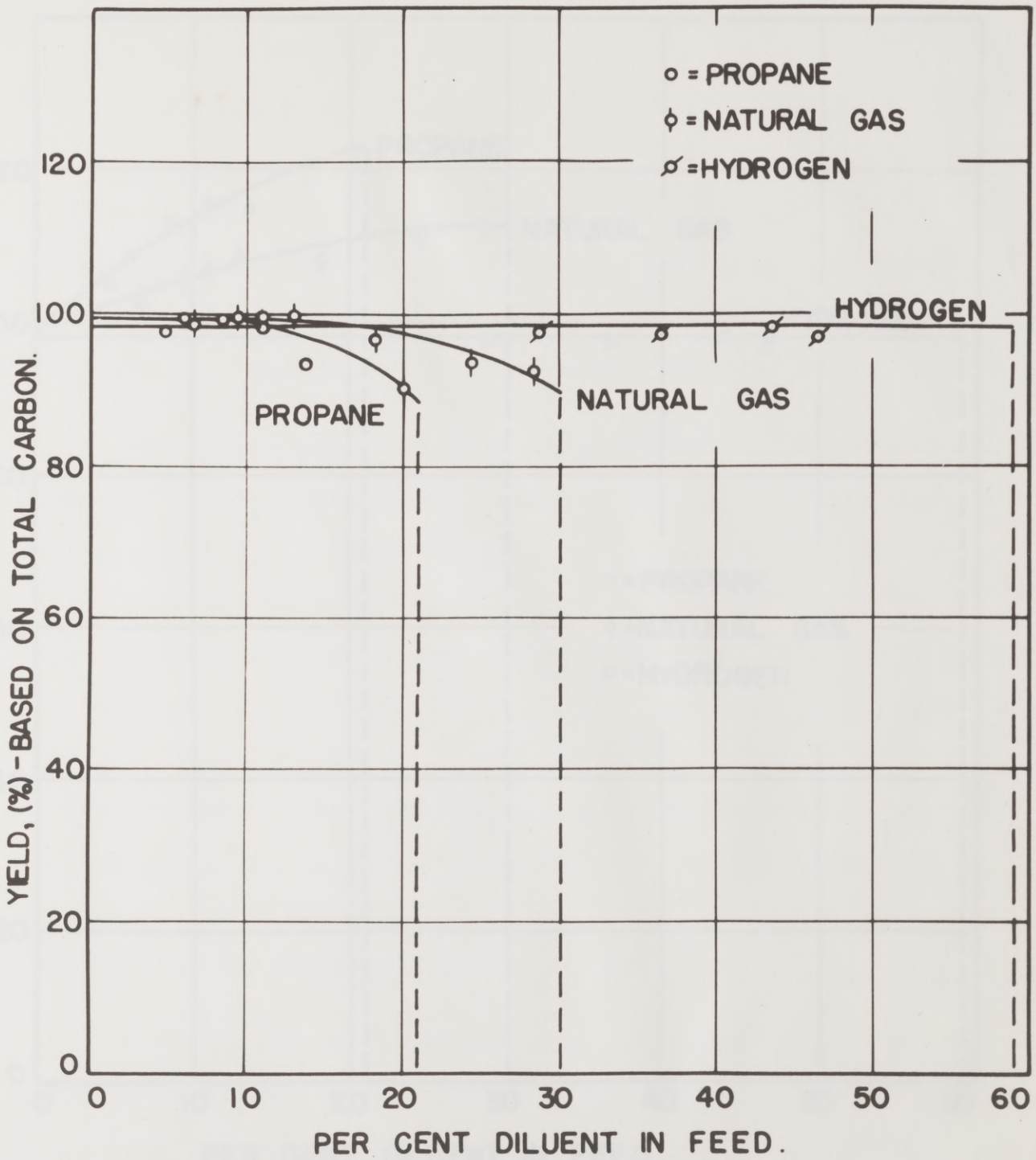


FIG. 10. VARIATION OF YIELD (BASED ON TOTAL CARBON) WITH FEED COMPOSITION.

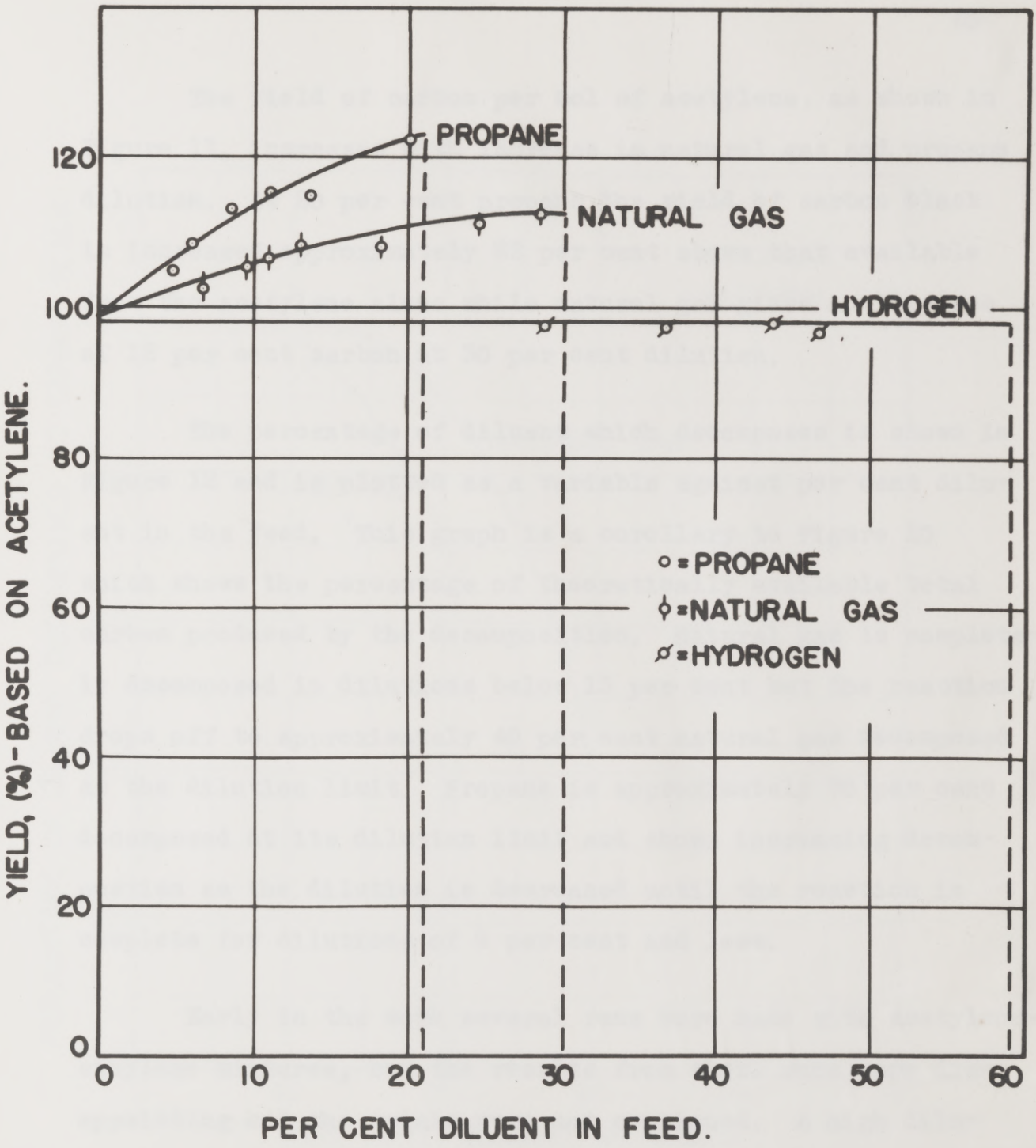


FIG. 11. VARIATION OF YIELD (BASED ON ACETYLENE) WITH FEED COMPOSITION.

The yield of carbon per mol of acetylene, as shown in Figure 11, increases with increase in natural gas and propane dilution. At 20 per cent propane the yield of carbon black is increased approximately 22 per cent above that available from the acetylene alone while natural gas gives an increase of 12 per cent carbon at 30 per cent dilution.

The percentage of diluent which decomposes is shown in Figure 12 and is plotted as a variable against per cent diluent in the feed. This graph is a corollary to Figure 10 which shows the percentage of theoretically available total carbon produced by the decomposition. Natural gas is completely decomposed in dilutions below 13 per cent but the reaction drops off to approximately 40 per cent natural gas decomposed at the dilution limit. Propane is approximately 70 per cent decomposed at its dilution limit and shows increasing decompostion as the dilution is decreased until the reaction is complete for dilutions of 9 per cent and less.

Early in the work several runs were made with acetylene-ethylene mixtures, but the results from these runs were disappointing and the trials were not continued. A high dilution of ethylene was expected since ethylene, as acetylene, has an exothermic decomposition reaction, but an upper limit of approximately 30 per cent was found. The results of these

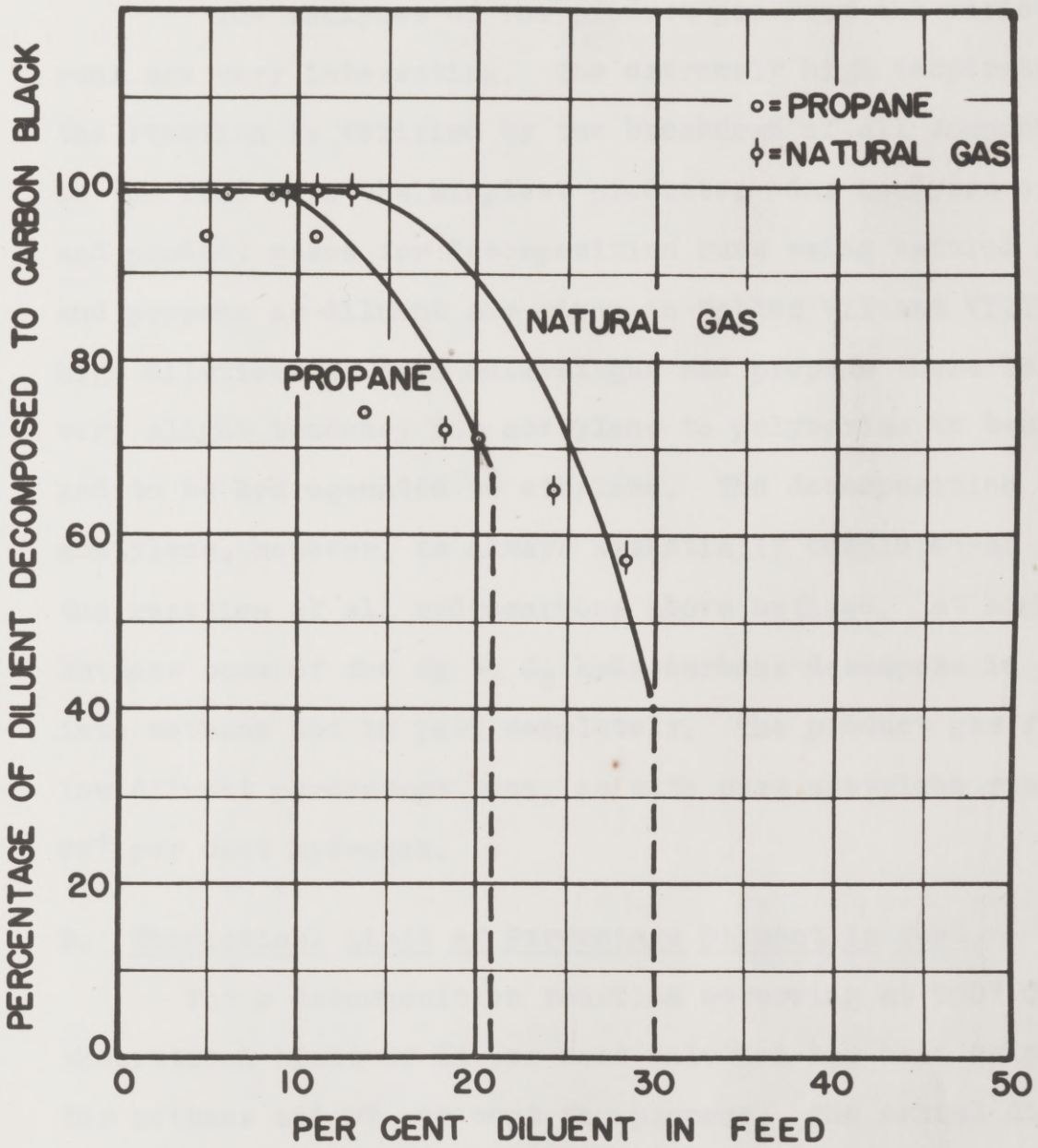


FIG. 12. VARIATION OF PERCENTAGE DILUENT DECOMPOSITION WITH FEED COMPOSITION.

trials are given in Table VI.

The analyses of the product gas from the various runs are very interesting. The extremely high temperature of the reaction is verified by the breakdown of all components in the feed into the simplest products. Gas analyses of feed and product gases for decomposition runs using natural gas and propane as diluent are given in Tables VII and VIII. At high dilutions of both natural gas and propane there is a very slight tendency for acetylene to polymerize to benzene and to be hydrogenated to ethylene. The decomposition of acetylene, however, is always essentially complete--as is the reaction of all hydrocarbons above methane. At high dilutions some of the C_2 to C_6 hydrocarbons decompose in part into methane and in part completely. The product gas from low diluent percentage runs, as with pure acetylene runs, is 98^+ per cent hydrogen.

B. Theoretical Limit of Percentage Diluent in Feed.

For a decomposition reaction occurring at 900° C., a theoretical limit of 54 per cent dilution has been calculated for methane and 37 per cent for propane. The actual dilution limits determined on the impure commercial gases are 30 per cent for methane and ~~28~~ 21 per cent for propane. The ratio of the actual limit to the theoretical in each case is 0.56. This ratio is expected to hold for other saturated hydrocarbon

TABLE VI

SUMMARY OF RESULTS ON ACETYLENE-ETHYLENE DECOMPOSITION RUNS

(10" d. Refractory)

Run No.	Acetylene Rate lb./hr.	Ethylene Rate lb./hr.	Volume % Ethylene	Comments
AE-3	18.3	3.88	16.5	Good decomposition as seen through windows.
"	18.9	4.96	19.6	
"	18.7	5.97	22.9	
"	19.7	6.49	23.5	
"	20.5	7.30	24.8	
"	17.7	8.34	30.4	C_2H_2 rate dropped slightly and decomposition stopped.
AE-4	18.5	6.01	23.2	Good decomposition.
"	18.9	7.60	27.2	
"	19.4	8.71	29.5	
"	19.3	9.44	31.2	
"	19.0	10.1	33.0	Partial decomposition with large clouds of "polymer smoke.
"	19.9	10.2	32.1	
AE-6	18.8(av.)	9.01(av.)	30.7(av.)	Decomposition seemed good all during the run. Very little "polymer." Dilution seems a little high, however.
	Yield = 82% (based on total carbon)			
	= 113% (based on acetylene)			
AE-7	19.7(av.)	7.20(av.)	25.3(av.)	Decomposition seemed very good. Very little "polymer."
	Yield = 91% (based on total carbon)			
	= 117% (based on acetylene)			

TABLE VII

MASS SPECTROGRAPH ANALYSES OF ACETYLENE-NATURAL GAS DECOMPOSITION RUN GASES

	Inlet Acetylene	Diluent Natural Gas	Product Gas JJ-119 13.0% Nat. Gas	Product Gas JJ-127 28.3% Nat. Gas
Hexanes	0	0.1	0	0
Hexenes	0	0.1	0	0
Benzene	0	0	0	0.1
Pentanes	0	0.4	0	0
Pentenes	0	T	0	0
Butanes	0	1.1	0	0
Butenes	0	ST	0	0
Butadiene	0	0	0	0
Propane	0	2.1	0	0
Propylene	0	0	0	0
Ethane	0	5.5	0	0.1
Ethylene	0	0	T	0.9
Methane	0	87.5	0.4	10.5
Methyl vinyl acetylene	0	0	0	0
Vinyl acetylene	0	0	0	0
Diacetylene	ST	0	0	0
Methyl acetylene	0	0	0	0
Acetylene	99.8	0.1	0	0.1
Carbon dioxide	0	2.0	0	0.1
Carbon monoxide	0	0.6	0.5	1.1
Water	0.2	0.5	0.8	0.8
Hydrogen	ST	0	98.3	86.3
Oxygen	0	0	0	0
Nitrogen	0	0	0	0

T = Trace = 0.03 - 0.04%

ST = Slight trace = 0.01 - 0.02%

TABLE VIII

MASS SPECTROGRAPH ANALYSES OF ACETYLENE-PROPANE DECOMPOSITION RUN GASES

	Inlet Acetylene	Diluent Propane	Product Gas JJ-131 8.5% Propane	Product Gas JJ-136 20.0% Propane
Benzene	0	0	0	0.3
Butanes	0	0.6	0	0
Butenes	0	T	0	0
Butadiene	0	0	0	0
Propane	0	89.5	0	ST
Propylene	0	0.6	0	0
Ethane	0	4.5	0	0.1
Ethylene	0	0	0.1	0.6
Methane	0	0	0.6	15.0
Vinyl acetylene	0	0	0	0
Diacetylene	ST	0	0	0
Methyl acetylene	0	0	0	0
Acetylene	99.8	0.9	0	0
Carbon dioxide	0	3.8	0	0
Carbon monoxide	0	0	0.3	0.4
Water	0.2	0.1	0.1	0.9
Hydrogen	ST	0	98.1	82.7
Oxygen	0	0	0	0
Nitrogen	0	0	0	0

T = Trace = 0.03 - 0.04%
ST = Slight trace = 0.01 - 0.02%

gases and would give an actual limit of decomposition for butane of 19 per cent since butane has a theoretical limit of 34 per cent. Ethylene, however, fails to conform to this rule and gives a ratio of 0.38. The experimental dilution limit of ethylene is approximately 31 per cent as given in Table VI, while the calculated limit is 82 per cent.

III. Calculation of Percentage Decomposition from Product Gas Analysis

Throughout the development of this work the yield from the decomposition reaction was determined by weighing the carbon produced. This method of yield calculation has two disadvantages:

1. Decomposition is often unsteady at the start of a run giving a widely fluctuating yield during this period. Several minutes of poor decomposition when averaged in over a run of 30 minutes gives a low yield which does not represent the true result. The percentage of acetylene decomposed during the unsteady period is not known and neither is the length of the period. A yield calculation based upon the weight of carbon black produced, consequently, is not representative of the percentage acetylene decomposed to carbon black during the steady period of the run.

2. Only one operating condition can be tested per run and at the end of the run the apparatus must be completely disassembled to be scraped free of carbon. This procedure is very time consuming and entails the risk of loss of carbon by hold-up in the apparatus.

After the unsteady period at the start of the run has passed, the decomposition goes smoothly and rate changes can be made without disturbing the reaction. The ideal operating condition for a test run is to be able to take an instantaneous reading and to determine the yield from this reading. By this method the yield is determined for any instantaneous rate without the yield being affected by any preceeding or following conditions. The feed rate(s) can then be changed and another reading taken. A method of calculation based upon (1) the change in volume of the feed gas as it undergoes reaction and (2) the analysis of the product gas is used to calculate the percentage acetylene decomposition into carbon and satisfactorily meets the requirements of accurate yield calculation and shorter test runs. An equation based upon this method of calculation is derived in the following section and was used to calculate the results given in the preceeding tables.

A. Derivation of the Equation of Decomposition Changes of Acetylene Alone.

1. Conditions: Acetylene from commercial cylinders is passed through charcoal adsorbers to remove the acetone in the gas. The exit gas from the adsorbers is metered and then fed into the decomposition chamber. Hydrogen is continuously flushed across the face of the burner during operation.

2. Incoming Gases: A mass spectrograph analysis of the acetylene after it has passed through the charcoal adsorbers shows 99.8 per cent acetylene and 0.2 per cent water. The feed gas can therefore be considered to be pure acetylene. The hydrogen flushing the burner face is also considered to be pure.

3. Gaseous Decomposition Products:

$$aC_2H_2 = bC_2H_2 + cH_2 + d(C_2H_2)_n^+ + e(C_2H_2)^\circ$$

$$fH_2(\text{burner}) = fH_2$$

where, a, b, c, ... = mols of gas

bC_2H_2 = unreacted acetylene

$(C_2H_2)_n^+$ = high boiling polymers which liquify or solidify before being metered. None have been found.

$(C_2H_2)^\circ$ = gaseous acetylene compounds other than acetylene itself.

4. Calculations:

Basis: 100 mols of inlet gases.

Hydrogen in product gas = c + f

$$c + f = (H_2)(1 + \Delta V)$$

where, $(H_2) = \frac{\text{mol. } H_2}{\text{mol. product gas}} = \frac{\%\ H_2 \text{ in product gas}}{1}$

ΔV = gas volume change during decomposition

= (gas leaving - gas entering)/gas entering

Then, $c = (H_2)(1 + \Delta V) - f$

Carbon formed = 2c

Theoretical carbon available = 2a

Yield = % of theoretical carbon

$$= \frac{2c}{2a} = \frac{c}{a}$$

$$= \frac{(H_2)(1 + \Delta V) - f}{a}$$

The slight volume change, ΔV, in the gas during decomposition is due to the formation of other gaseous substances by side reactions. No evidence has been found of the formation of either liquids or solids.

B. Decomposition Equation for Mixtures of Acetylene and Other Gases

A similar equation can be derived for the decomposition of mixtures of acetylene with diluent gases. The equation would be very long and its derivation quite laborous when

natural gas or commercial propane is used unless simplifications were made since each diluent contains a large number of compounds. The natural gas used as diluent contains all saturated hydrocarbons from C_1 to C_5 and the theoretically possible products of the thermal reaction of these components are numerous. Methane, however, is the only saturate found in the product gas in greater quantity than several tenths of a per cent and ethylene is the only unsaturate of significance. The product gas from the decomposition of acetylene-propane mixtures is quite similar. The equation will be derived with the simplification that pentanes, butanes, propane and ethane decompose into carbon and hydrogen, that methane is sometimes only partially decomposed, that carbon dioxide goes to carbon monoxide, and that water is unchanged. The products of natural gas and propane are:

In		Out	Theoretical Carbon	Carbon Formed
gC_5H_{12}	=	$6gH_2$	5g	5g
hC_4H_{10}	=	$5hH_2$	4h	4h
iC_3H_8	=	$4iH_2$	3i	3i
jC_3H_6	=	$3jH_2$	3j	3j
kC_2H_6	=	$3kH_2$	2k	2k
sCH_4	=	$mCH_4 + nH_2$	~~n/2~~ s	~~s~~ $\frac{n}{2}$
pCO_2	=	$2pCO$	-	-
qCO	=	qCO	-	-
rH_2O	=	rH_2O	-	-
aC_2H_2			2a	2a, (very close)

$$\text{Total carbon formed} = 5g + 4h + 3i + 3j + 2k + n/2 + 2a$$

$$\text{but, } n/2 = s - m \quad ; m = (CH_4)(1 + \Delta V)$$

$$= s - (CH_4)(1 + \Delta V)$$

$$\text{Total carbon formed} = 5g + 4h + 3i + 3j + 2k + 2a + s - (CH_4)(1 + \Delta V)$$

$$\text{Yield} = \frac{\text{Total carbon formed}}{\text{Theoretically available carbon}}$$

$$= \frac{5g + 4h + 3i + 3j + 2k + 2a + s - (CH_4)(1 + \Delta V)}{5g + 4h + 3i + 3j + 2k + s + 2a}$$

All terms in the above equation are known except the change in volume, ΔV, of the gas as it undergoes reaction. The terms a to s are components of the feed gas and are determined by analysis while ΔV is calculated using the equation below. The methane term is: (CH_4) = % methane in product gas.

Basis: 100 mols of inlet gas.

$$\Delta V = \frac{\text{Volume out - Volume in}}{\text{Volume in}}$$

$$= \frac{(b + c + e + f + 6g + 5h + 4i + 3j + 3k + m + n + 2p + q + r)}{100}$$

$$- \frac{(a + f + g + h + i + j + k + s + p + q + r)}{100}$$

Using the simplifying equations

$$b + c + e = a, \text{ (very close)}$$

$$s = m + n/2$$

$$m = (CH_4)(1 + \Delta V)$$

the equation solves to the form

$$\Delta V = \frac{5g + 4h + 3i + 2j + 2k + p + s - (CH_4)}{100 + (CH_4)}$$

Using analyses of the feed gas and the product gas, the carbon black formed in the decomposition reaction can be calculated. The calculation made in this way is limited by the accuracy of the gas analyses and by any error in metering when the acetylene is mixed with a diluent, but it has the advantage of giving an instantaneous value. The above mentioned inaccuracies are usually small and have little effect upon the calculation.

C.

Sample Calculations

1. Pure Acetylene.

Run NN-3. Gas Sple. JJ-84.

Inlet Gases: $C_2H_2 = 88.4\% = a$

Burner $H_2 = \frac{11.6\%}{100.0\%} = f$

Product Gas: $H_2 = 99.2\%$ (Table II)

$\Delta V = -0.01$ (A 1% loss in acetylene through side reactions is assumed although it is probably less. Product gas rate measurements are not accurate due to apparatus static pressure changes and leakage. Gas volume change as calculated from inlet and outlet gas rates usually varies from 2 to -3%.)

$$\text{Yield} = \frac{(H_2)(1 + \Delta V) - f}{a}$$

$$= \frac{(99.2)(0.99) - 11.6}{88.4}$$

$$= 98.1\%$$

2. Propane.

Run APNN-1. Gas Sple. JJ-131.

Inlet Gases: C_2H_2 = 83.7% = a

Burner H_2 = 8.5%

Propane = 7.8%

100.0%

Commercial Propane:

C_4H_{10}	= 0.6 = h';	4h' =	2.4	(h' = % C_4H_{10} in propane.
C_3H_8	= 89.5 = i';	3i' =	268.5	h = % C_4H_{10} in inlet gases.)
C_3H_6	= 0.6 = j';	3j' =	1.8	
C_2H_6	= 4.5 = k';	2k' =	9.0	
CH_4	= 0 = s';	s' =	0.0	
C_2H_2	= 0.9 = a';	2a' =	1.8	
			283.5	

CO_2 = 3.8 = p'.

$$(5g + 4h + 3i + 3j + 2k + 2a_{(\text{propane})} + s)$$

$$= (283.5)(\% \text{ propane in inlet gases})$$

$$(5g + 4h + 3i + 2j + 2k + p + s)$$

$$= (284.9)(\% \text{ propane in inlet gases})$$

Product Gas: (CH_4) = 0.6% (Table VIII)

$$V.C. = \frac{(5g + 4h + 3i + 2j + 2k + p + s) - (CH_4)}{100 + (CH_4)}$$

$$= \frac{(284.9)(0.078) - 0.6}{100 + 0.6}$$

$$= 0.215$$

$$\text{Yield} = \frac{(5g + 4h + 3i + 3j + 2k + s) + 2a - (CH_4)(1 + V.C.)}{(5g + 4h + 3i + 3j + 2k + s) + 2a}$$

$$= \frac{(283.5)(0.078) + 2(83.7) - 0.6(1.215)}{(283.5)(0.078) + 2(83.7)}$$

$$= 99.6\% \text{ (based on total carbon)}$$

$$= \frac{\text{(as above)}}{2(83.7)}$$

$$= 112.8\% \text{ (based on acetylene).}$$

HISTORY OF THE DEVELOPMENT OF ESSENTIAL STRUCTURAL PARTS

I. Development of the Burner and Refractory

In the literature survey undertaken before this work was started, a patent on a "Process of Making Carbon Black" was found which was granted to the Canada Carbide Company, Limited, of Shawinigan Falls, Province of Quebec, Canada. The patent described a method for the production of carbon black by the thermal decomposition of acetylene. As a first step in the project it was though wise to follow the equipment design as outlined in this patent. To our knowledge, the patent was never applied for in the United States and the Canadian patent was to expire in 1945--six months following the beginning of this work.

The patent gave no apparatus dimensions, no gas flow rates, and only a sketchy outline of operating conditions. It was therefore necessary to assume dimensions for the apparatus to be constructed. The refractory which was built had a length of 12 inches, an inside diameter of 2 inches, and a wall thickness of 1 inch, while the burner consisted of a 3/8-inch diameter acetylene inlet tube, an annular space for admitting air, and a water jacket. The refractory was heated by the combustion of acetylene admitted through the central tube with air entering through the annular space. When the

refractory had been heated to approximately 1000° C., the air rate was lowered and the acetylene throughput adjusted to some desired value. If the air was cut off completely there was no carbon formation, but if approximately 40 per cent of the theoretical air for combustion of the acetylene was admitted, 10 per cent of the acetylene was decomposed. Coke would form on both the refractory wall and the face of the burner and decomposition would stop when the coke mass grew until it extended across the inlet acetylene tube.

Work on this apparatus was soon stopped, but the patent was reviewed at a later date after a workable burner and refractory had been designed. The apparatus dimensions and acetylene throughput, which had been carefully omitted from the patent, were found to be very critical. The patent is workable only if information not disclosed by the patent itself is known.

The formation of coke on the refractory wall and on the burner face was of the greatest hindrance. Often both types of coking would occur simultaneously, but each was independent of the other and could take place alone. Sometimes the coke body would fall from its own weight or from the force of the incoming acetylene, but if the coke remained and grew until it covered the acetylene tube, it would stop the decomposition. The acetylene would continue to flow and some

polymerization would occur from the heat within the refractory, but it would not decompose. If coke forms on the burner, a "bee hive" of coke grows out from the burner face. The general shape of the coke body is shown in Figure 13 (a) and details of several coke "hives" are shown in the photographs in Figure 13 (c). The coke attaches to the face of the water jacket and each coke body has the same general shape. The coke which forms on the refractory is often not attached directly to the refractory wall, but grows upon a layer of spongy carbon as shown in Figure 13 (b). The layer of spongy carbon forms in the refractory whether coking does or does not occur. Each type of coking gives the same undesirable result, but each was attacked and solved individually.

The following hypothesis is given for coke formation on the burner face. A small amount of acetylene polymer exists in the gas inside the refractory. This polymer condenses on the water-cooled burner face and is progressively dehydrogenated to coke. The coke entrains acetylene which in turn is polymerized and dehydrogenated to form more coke. Similarly, coke formation on the refractory always starts on the "cool" top section which has not been heated sufficiently by the heat-up flame. The "cool" section of the refractory can furnish enough heat to polymerize the acetylene, but not enough to decompose it. The cycle of polymerization and dehydrogenation is started here, too. Coking on the refractory

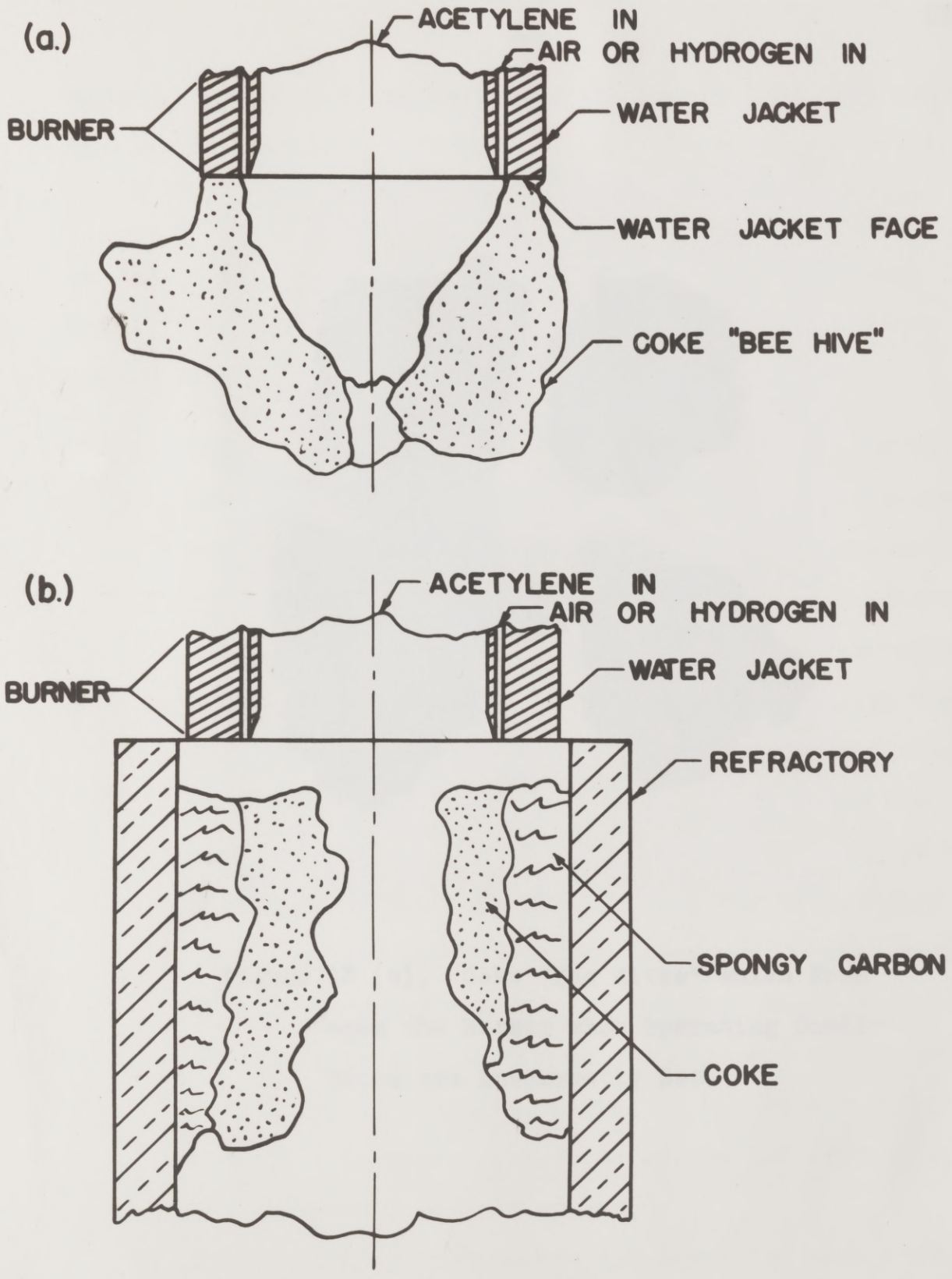


FIG. 13. COKE FORMATION.

Figure 13 (c). Coke "Bee Hives" which Form upon the Burner when Operating Conditions are Incorrectly Set.

does not occur when the refractory is heated "red hot" all the way to the top.

The most logical manner of decomposing acetylene seemed to be to introduce it into a preheated refractory. Hence, this part of the procedure outlined in the Canadian patent was continued with the following modifications:

1. The Canadian patent stated that from 0.1 to 1.0 per cent of theoretical air is required to make the decomposition continuous, however, a much larger percentage was found necessary (with a 2 inch inside diameter refractory) to keep the decomposition going. Since nitrogen in the air was thought to dilute the acetylene to such an extent that decomposition was hindered, oxygen, instead of air, was used in the next trial, but coke formation then occurred at the acetylene-oxygen interface, i. e., the coke formed on the end of the tube which forms the annular space for the incoming oxygen. It was then found that, if this interface is separated from the end of the tube by a layer of hydrogen, coking on the burner face is stopped. However, coke formation on the refractory was unaffected by this change.
2. Burner tips of both quartz and soapstone were tried in an attempt to prevent coke formation on the burner. Both trials failed.

3. A burner was designed to give a sharp jet of acetylene into the refractory. The jet of acetylene prevented coking on the burner, but not on the refractory.
4. Hydrogen was premixed with acetylene; this delayed coking, but did not prevent it.
5. A small acetylene-air pilot flame was placed at right angles to the main body of acetylene several inches below the main burner. The pilot flame continued to burn throughout the run. This was due to the thought that perhaps a more violent means than a hot refractory was needed to start, and perhaps continue, the acetylene decomposition. This served to improve carbon formation, but did not stop coking.
6. The system was placed under a pressure of 5 to 35 psg. and runs were made both with and without a pilot flame. Carbon was formed in small amounts, but coke again formed inside the refractory and stopped decomposition.

By this time several methods of avoiding coke formation on the burner face had been found, but no method was known to prevent its formation on the refractory. Attempts were next made to operate with several types of apparatus which contained no refractory:

1. Acetylene was jetted into hot flue gases from the combustion of a hydrogen-methane-air mixture. No carbon was formed.
2. A decomposition chamber was made of ¼-inch iron pipe. The pipe was heated several minutes, the pressure raised to 25 psig., and acetylene admitted. A little carbon plus very hard coke was formed.
3. A decomposition chamber of 1-inch iron pipe was constructed. The chamber was preheated with a hydrogen-oxygen flame and acetylene then admitted while the flame continued to burn. The system pressure was varied from atmospheric to 40 psig. No carbon was formed.

A survey of the work done thus far revealed the following facts.

1. The use of a preheated refractory gave the best decomposition.
2. Placing the system under pressure gave only slightly better results than did runs made at atmospheric pressure.
3. The formation of coke must be prevented to get continuous acetylene decomposition.

Additional runs were then made using a refractory decomposition chamber and with the system under atmospheric

pressure. The burner design shown in Figure 14 was used. This design incorporated the following features:

1. The inlet acetylene tube was water cooled to minimize acetylene polymerization.
2. The water jacket was made narrow to reduce the water-cooled burner face. It was on this section of the burner that coke formed.
3. Air was added in an annular space outside the water jacket. The air tended to flush acetylene away from both the water-cooled burner face and from the upper refractory wall. An amount of air sufficient to completely flush acetylene from these parts, however, would stop decomposition.

A small amount of carbon could be made using this apparatus and occasionally a run was made without formation of coke. This, finally, was the beginning of the development of the decomposition process. Larger refractories were then used with the same type of burner. The percentage acetylene decomposed increased as the refractory diameter was increased but coking would still occur. The addition of air along the refractory wall and the use of larger refractories delayed the coking to such an extent that runs of length sufficient to calculate yields could be made. Continuous runs, however, were still impossible. The following conditions were observed

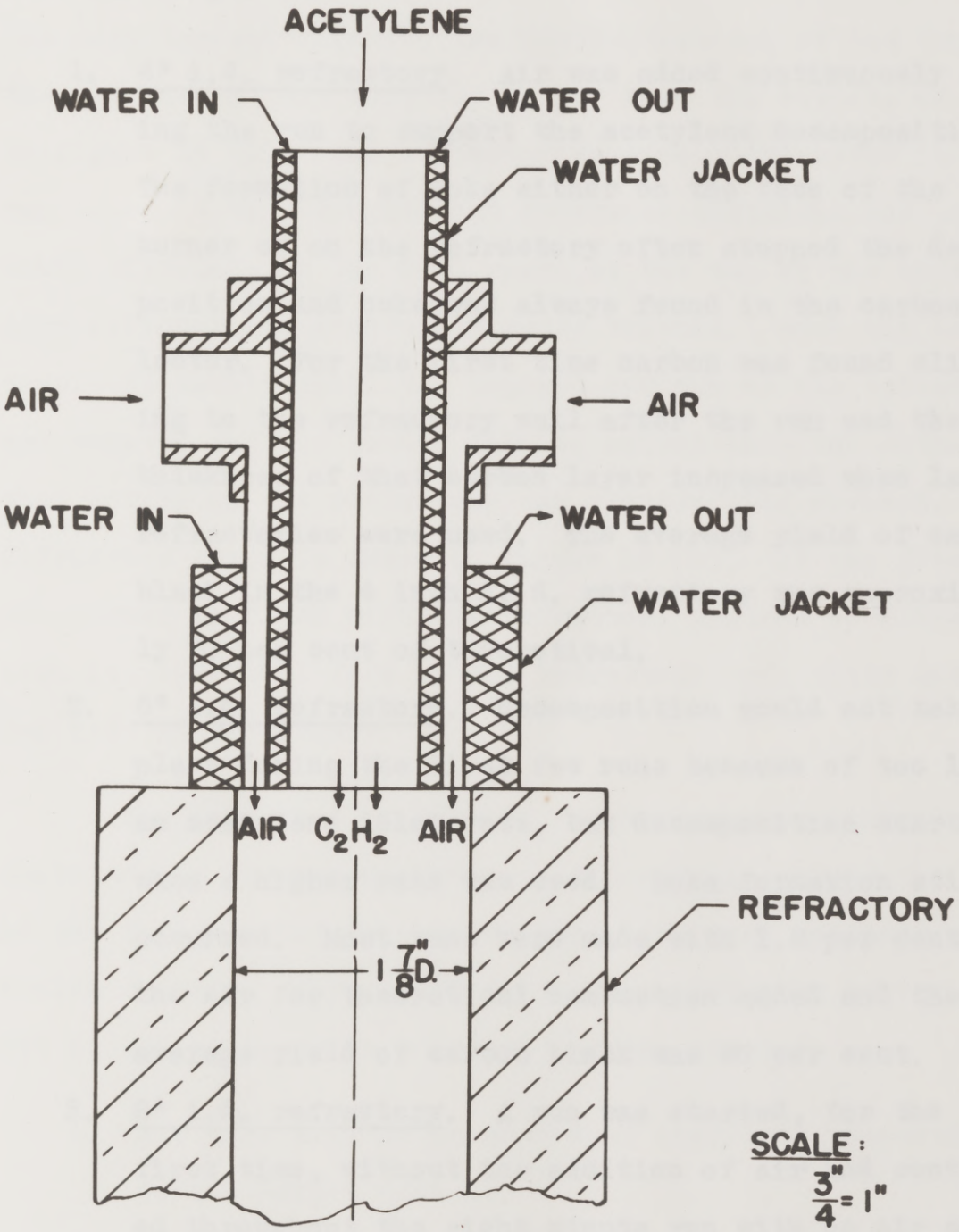


FIG. 14. BURNER DEVELOPMENT.

with the larger refractories.

1. 4" i.d. refractory. Air was added continuously during the run to support the acetylene decomposition. The formation of coke either on the face of the burner or on the refractory often stopped the decomposition and coke was always found in the carbon collector. For the first time carbon was found clinging to the refractory wall after the run and the thickness of that carbon layer increased when larger refractories were used. The average yield of carbon black in the 4 inch i. d. refractory was approximately 70 per cent of theoretical.
2. 6" i.d. refractory. Decomposition would not take place during the first few runs because of too low an acetylene inlet rate, but decomposition started when a higher rate was used. Coke formation still occurred. Most runs were made with 1.2 per cent of the air for theoretical combustion added and the average yield of carbon black was 80 per cent.
3. 8" i.d. refractory. A run was started, for the first time, without the addition of air and continued throughout the eight minute run with no air added. Coke still formed. The yield of carbon black was an average of 90 per cent.

All refractories were built with the top two inches of the core tapered--leaving the inside diameter at the top of the refractory just slightly larger than the burner, as shown in Figure 15 (a). The refractories were constructed in this way since it was thought that otherwise acetylene and polymer would circulate in the dead space at the top of the refractory cylinder and eventually cause trouble. Such was not the case. It wasn't until the tapered section of the refractory was removed and the burner made to extend into the refractory that coking on the refractory was successfully avoided. This refractory shape is shown in Figure 15 (b). If the face of the burner is flush with the refractory instead of extending into it, coke will form on the refractory and bridge across the face of the burner.

The formation of coke on the burner was eliminated by continuously blowing a stream of "inert" gas across the face of the water jacket to prevent acetylene from contacting this cooled surface. Air was first used to flush the burner face, but it was replaced by hydrogen for two reasons:

1. Air will consume an amount of acetylene proportional to its oxygen content.
2. The product gas of the decomposition is hydrogen. Its recovery is facilitated by using hydrogen to flush the face of the burner instead of another gas.

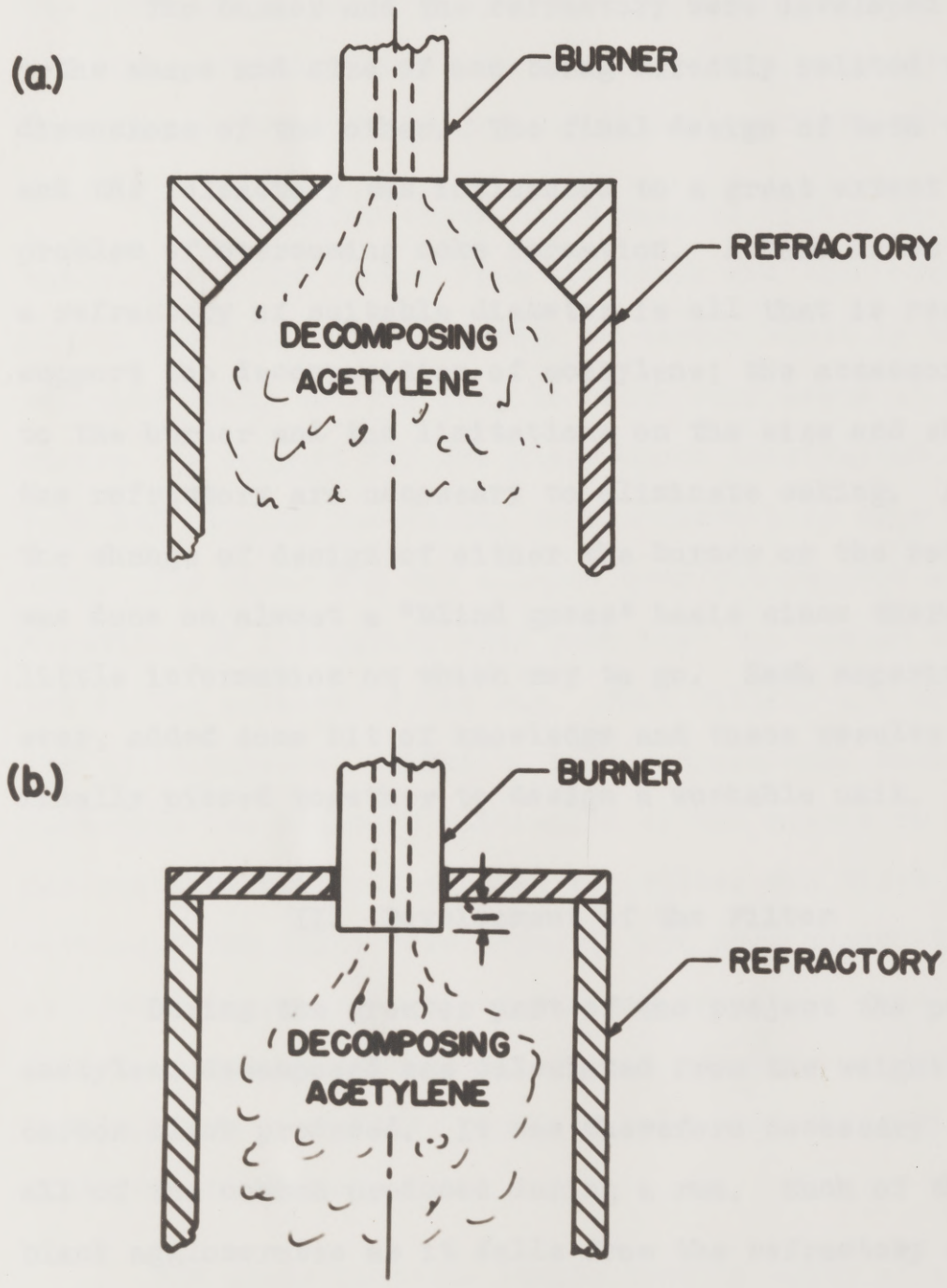


FIG. 15. REFRACTORY DEVELOPMENT.

The burner and the refractory were developed together --the shape and size of one being directly related to the dimensions of the other. The final design of both the burner and the refractory was influenced to a great extent by the problem of overcoming coke formation. A bare inlet pipe and a refractory of suitable diameter is all that is required to support the decomposition of acetylene; the accessories added to the burner and the limitations on the size and shape of the refractory are necessary to eliminate coking. At times the change of design of either the burner or the refractory was done on almost a "blind guess" basis since there was so little information on which way to go. Each experiment, however, added some bit of knowledge and these results were finally pieced together to design a workable unit.

II. Development of the Filter

During the greater part of the project the per cent of acetylene decomposed was calculated from the weight of the carbon black produced. It was therefore necessary to recover all of the carbon produced during a run. Much of the carbon black agglomerates as it falls from the refractory and is easily collected, but the "fines" are carried by the gas stream. It was thought highly desirable to filter the carbon from the hot gas and not resort to either cooling or quenching prior to carbon removal, since any acetylene polymer in

the product gas would deposit on the carbon during the cooling step. Foreign materials adsorbed on a carbon black affect its properties and greatly limit its field of usefulness.

The Fiberglas cloth first used to filter the hot gas was simply a bag formed from the cloth and tied over the end of the gas line. The recovery of carbon black by this method was excellent, but the fragile cloth soon broke at points of stress. A support for the glass cloth constructed of steel rods and greatly resembling an elongated bird cage was then made. The cloth bag was slipped over the support and the direction of filtration made such that the carbon was collected on the outside of the bag. This filter, and several of its modifications, failed to give satisfactory service under prolonged use although filtration of the carbon by each filter was always excellent when the filter was first placed in service. The cloth tore after it had aged since it vitrifies at elevated temperature and becomes brittle. This type of filter was placed inside the carbon separator so that carbon falling from the filter could be collected along with the agglomerated carbon.

The glass cloth no longer tore in spite of its aging when it was supported so that no flexing could occur. This was done by wrapping the cloth around a perforated 6-inch diameter pipe as explained in the section on "Apparatus."

The glass cloth is undoubtedly partially vitrified as it was with other filters, but its use as a filtration medium is unaffected by the vitrification. A firm, fine mesh support is necessary to prevent the brittle cloth from failing.

THEORY OF THE ACETYLENE THERMAL DECOMPOSITION REACTION

It is with a feeling of rashness that a theoretical study of the decomposition of acetylene is undertaken. A study of the mechanism and kinetics of acetylene reactions has been long avoided by workers in these fields--this decision being amply justified by both the high reactivity of the acetylene and its complicated chemical structure. Since the work done here does give some clue to the type of reaction occurring in the decomposition of acetylene, the mechanism of this reaction is discussed with the hope that it will give support to any future work done in this field.

All measurements in this work were made with the aim of calculating the yield of carbon black while all kinetic discussions of reactions deal with the rate of reaction. The rate is defined as:

$$\text{Rate of reaction} = -\frac{dx}{dt} = \frac{\text{mols of acetylene decomposed}}{(\text{unit volume})(\text{unit time})}$$

In a flow process the reaction time can be made constant for reaction chambers of various cross-sections by keeping the gas velocity constant and a unit volume of gas within the reaction chamber can be assumed. With these conditions the rate of reaction, as defined in the above equation, is proportional to the yield. The following discussion will,

therefore, consider the terms "rate" and "yield" to be interchangeable with the understanding that one is directly proportional to the other.

I. Type of Reaction Mechanism

The thermal decomposition of acetylene is considered to be a chain reaction as against a reaction perpetuated by thermal activation alone. The following results are cited in support of this statement.

A. Effect of Refractory Diameter

The yield from the decomposition of acetylene increases with refractory diameter until a limiting decomposition is reached. A thermally activated reaction should not be affected by changes in refractor diameter while a well known criterion of many chain reactions is an increase in the rate of change with increase in the dimensions of the vessel, due to the longer path to be traversed before the reaction reaches the wall.

B. Effect of Input Rate

If the decomposition reaction is proceeding quietly and the acetylene input rate is continuously decreased, the decomposition suddenly stops. The yield holds constant at a high percentage until the decomposition breaks; it does not show a tapering off as the rate is lowered. A thermally

activated reaction does not exhibit such sudden changes. This lower limit of input rate seems to indicate a condition where the chains are destroyed more rapidly than they react due to the slow acetylene input. The lack of sufficient acetylene molecules to propagate the chains allows the reaction to stop.

C. Effect of Inert Diluent

A very sharp limit of decomposition is also found when a diluent is added to acetylene in increasing proportions. A point is reached where a slight increase in diluent rate completely stops the reaction and again reduces the yield from a high value to zero. This condition corresponds to the destruction of chains within the gas phase by collision of the activated complex with a third body. The very sharp limit of decomposition is a characteristic of branched chains in contrast to straight chains. Chain-breaking exceeds chain-branching at this limit.

Hydrogen in a ratio as high as 1:1 can be used to dilute acetylene without affecting the yield of carbon black. A sharper upper limit of dilution is again found and corresponds to the condition discussed in the preceeding paragraph. The almost negligible influence of an inert gas up to the point where it sharply stops the reaction is a criterion of many chain reactions.

II. Proposed Reaction Mechanism

The following mechanism for the thermal decomposition of acetylene is here proposed:

Chain Forming $\quad HC\equiv CH \overset{x_1}{=} \overset{k_1}{} H \overset{x_2}{} + C\equiv CH \overset{x_3}{} \quad$ ---(a).

Chain Propagating $\quad H \overset{x_2}{} + HC\equiv CH \overset{x_1}{} = \overset{k_2}{} H_2 + C\equiv CH \overset{x_3}{} \quad$ ---(b).

" " $\quad C\equiv CH \overset{x_3}{} = \overset{k_3}{} H \overset{x_2}{} + C\equiv C \quad$ ---(c).

Chain Breaking $\quad H \overset{x_2}{} + C\equiv CH \overset{x_3}{} + W = \overset{k_4}{} HC\equiv CH \overset{x_1}{} + W \quad$ ---(d).

" " $\quad H + H + W = H_2 + W \quad$ ---(e).

Chain Branching $\quad H + HC\equiv CH = H + H + C\equiv CH \quad$ ---(f).

where; $x_1, x_2, \ldots$ = concentration

$k_1, k_2, \ldots$ = rate constant

W = wall effect

For calculations, use Eq. (d) as the chain breaking step. It is essentially equivalent to Eq. (e) since at

equilibrium $x_2 = x_3$.

$$-\frac{dx_1}{dt} = k_1x_1 + k_2x_1x_2 - k_4x_2x_3W \qquad ---(1a).$$

$$\frac{dx_2}{dt} = 0 = k_1x_1 - k_2x_1x_2 + k_3x_3 - k_4x_2x_3W \qquad ---(2a).$$

In Eq. (2a), $k_2x_1x_2 = k_3x_3$

since rate of formation = rate of decomposition of C≡CH

Then, $k_1x_1 = k_4x_2x_3W$

Also, $x_2 = x_3$

So, $k_1x_1 = k_4x_2^2W$

$$x_2 = (k_1x_1/k_4W)^{\frac{1}{2}}$$

In Eq. (1a), k_1x_1 and $k_4x_2x_3$ may be neglected as small with the assumption that the chains are long, i.e., that reactions (b) and (c) occur many times more than reactions (a) and (d).

$$-\frac{dx_1}{dt} = k_2x_1x_2 \qquad ---(1b).$$

Substituting (2c) into (1b):

$$-\frac{dx_1}{dt} = k_2 x_1 (k_1 x_1 / k_4 W)^{\frac{1}{2}}$$

$$= k' x_1^{1.5} / W^{\frac{1}{2}} \qquad \text{---(1c).}$$

For any refractory (W = constant), the rate of the reaction by the above mechanism is proportional to the 1.5 power of the acetylene concentration.

The wall effect, W, depends upon the wall area per unit gas volume.

$$\text{Then, } W = \frac{\text{wall area}}{\text{gas volume}} = \frac{\pi dh}{\frac{\pi d^2 h}{4}} = \frac{4}{d}$$

Substitution of this value for W into Eq. (1c) gives:

$$-\frac{dx_1}{dt} = k''(d)^{\frac{1}{2}} \qquad \text{---(1d).}$$

since the acetylene concentration (x_1) is held constant artifically during the reaction by the continued addition of reactant. Eq. (1d) may be arranged to give the following relation:

$$\text{Yield} = k'''(d)^{\frac{1}{2}} \qquad \text{---(1e).}$$

The ratio of yield to the square root of the diameter should therefore be a constant value of any cylinder type refractory

where chain-breaking occurs at the wall.

The variation of yield with refractory diameter is summarized in Figure 8 and is tabulated in Table IX. The Yield/$(d)^{1/2}$ ratio given in the final column of Table IX is constant within experimental variation and correlates well with the prediction of Eq. (1e). The gas volume diameter is used in the calculations since obviously the layer of carbon on the refractory forms the actual wall of the reaction chamber. The relationship breaks down for gas volume diameters larger than 7 inches which indicates that chain-breaking at the wall no longer influences the reaction in large diameter refractories.

TABLE IX

CALCULATION OF YIELD/$(d)^{1/2}$ RATIO

Actual Refractory Diameter, Inches	Gas Volume Diameter, d, Inches	Yield, %/100	$\frac{\text{Yield}}{d^{1/2}}$
4	4	0.72	0.360
6	5	0.80	0.358
8	6	0.91	0.371
10	7	0.97	0.366

The constancy of the Yield/$(d)^{1/2}$ ratio gives proof that the chain-breaking reaction occurs at the wall, but gives no indication that the remainder of the postulated mechanism is correct. The chain-forming reaction, Step (a), is assumed to occur by breaking a C-H bond in preference to breaking the C≡C bond. The energy of activation for breaking each bond can be approximated by using an empirical equation derived by Fugassi and Warrick[7] for gaseous unimolecular reactions.

$$E = 2.858\bar{\nu} (35.5 - 900.45\bar{\nu}/D).$$

where, E = energy of activation in calories.

$\bar{\nu}$ = frequency of bond in wave numbers ($cm.^{-1}$).

D = heat of dissociation (bond energy) in calories.

The calculation of activation energy using this equation is summarized in Table X.

It appears that the activation energy for breaking the C-H bond is 39 kcal./g. mol. lower than the energy for breaking the C≡C bond. This means that the former proceeds at a rate approximately

$$e^{E/RT} = e^{39,000/(2)(1300)}$$

$$= 10^{39,000/2.3(2)(1300)} = 10^{6.5}$$

times as fast as the latter at 1000° C. The difference in

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[7] Fugassi, Paul and Warrick, Earl, "The Empirical Correlation of Activation Energies of Gaseous Unimolecular Reactions with Vibrational Frequency," J. Phy. Chem. 46, 630 (1942).

TABLE X

ACTIVATION ENERGY FOR DISSOCIATION

Bond	$\bar{\nu}$, ($cm.^{-1}$)	D, calories	E, kcal./g.mol.
C-H	1974 [8]	92,000 [9]	91
C≡C	3374 [8]	138,000 [10]	130

rate lessens if the reaction takes place at a higher temperature, but the dominance of the C-H break is still great.

The chain-propagating reactions consist of the consumption and regeneration of the atomic hydrogen chain carrier. Molecular hydrogen is produced in one reaction and carbon in the other. Lewis and von Elbe[11] postulate a similar mechanism for the initial step in the oxidation of acetylene,

$$OH + C_2H_2 = C{\equiv}CH + H_2O$$

[8] Herzberg, Gerhard, Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Company, Inc., New York, 1945, p. 288.

[9] Daniels, Farrington, "Prediction of Reaction Rates," Ind. Eng. Chem. 35, 504 (1943).

[10] Henkin, H. and Burton, M., "Bond Strength and Potential Energy Relationships in Acetylene," J. Chem. Phys. 8, 297 (1940).

[11] Lewis, B. and von Elbe, G., Combustion, Flames and Explosions of Gases, Cambridge University Press, London, 1938, p. 122.

while Peters and Wagner[12] conclude that the decomposition of acetylene follows the steps

$$HC{\equiv}CH = -C{\equiv}C- = \text{Solid C.}$$

The $C{\equiv}C$ radical can decompose into elementary carbon or perhaps remain in the polymerized C_2 state. The occurence of the C_2 radical has been verified.[13]

In large diameter refractories the wall effect, W, becomes negligible and Eq. (1c) reduces to

$$\frac{-dx_1}{dt} = k_2 x_1 (k_1 x_1 / k_4)^{1/2}$$

$$= k' x_1^{1.5} \qquad \text{---(1d).}$$

Then,

$$k' = k_2 (k_1 / k_4)^{1/2} \qquad \text{---(4a).}$$

$$\ln k' = \ln k_2 + 1/2 \ln k_1 - 1/2 \ln k_4 \qquad \text{---(4b).}$$

From Arrhenius' equation:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

$$\ln k = \frac{-E}{RT}$$

---

[12] Peters and Wagner, Zeit. f. Phys. Chem. 153 A, 161; Willey, E. J. B., "Free Radicals in the Electric Discharge," Trans. Far. Soc. 30, 230 (1934).

[13] Lewis and von Elbe, op. cit., p. 128 and Peters and Wagner, loc. cit.

Substituting into (4b):

$$E' = E_2 + 1/2E_1 - 1/2E_4$$

where, E' = activation energy of the overall reaction.

E_1, E_2, E_4 = activation energy of Step (a), Step (b), and Step (d).

E_1 = 91 k.cal./g. mol.

E_2 = 15 "

E_4 = 5 "

E_2 and E_4 have assumed values which correspond to values determined experimentally for similar reactions.[14]

$$E' = 15 + 91/2 - 5/2$$
$$= 58 \text{ k.cal./g. mol.}$$

The activation energy of the overall reaction, E', can be substituted into the Arrhenius equation and the specific reaction rate calculated.

$$k = Ae^{-E'/RT}$$

Assume the reaction to take place at 1000° C. and $A = 10^{12}$. The constant, A, has a value varying from 10^{11} to 10^{13} for first and second order reactions, consequently, a value of 10^{12} for a 1.5 order reaction seems to be a correct assumption.

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[14] Rice, F. O. and Herzfeld, K. F., "The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals," Jour. Am. Chem. Soc. 56, 284 (1934).

$$k = 10^{12} \cdot e^{-58,000/(2)(1300)}$$

$$= 2.1 \cdot 10^{2} \text{ sec.}^{-1}(\text{g. mol./cc.})^{-1/2}$$

Then, $\frac{dx}{dt} = kx^{1.5}$

where, $x = (1/22,400)(273/1300)$ g. mol./cc.

$$\frac{dx}{dt} = (2.1 \cdot 10^{2})(1/22,400)^{1.5}(273/1300)^{1.5}$$

$$= 6.3 \cdot 10^{-6} \text{ g.mol./(cc)(sec.)}$$

(Calculated reaction rate).

The instantaneous concentration of acetylene within the refractory is constant regardless of the input rate since the instantaneous concentration depends, in this case, only upon the temperature and pressure of the reactant. Since essentially 100 per cent of the acetylene is decomposed, the reaction rate can be calculated as follows:

Reactant pressure = 1 atm. abs.

Reactant temperature = 1300° K.

Reactant input rate = m/s = g. mol./sec.

Reactant volume = (22,400)(m)(273/1300), cc. ← Reverse

Rate of reaction = $\frac{dx}{dt} = \frac{m/s}{(22,400)(m)(273/1300)}$ ← Rev.

Let, s = 1 sec.

Then,

$$\frac{dx}{dt} = 9.3 \cdot 10^{-6} \text{ g. mol./(cc.)(sec.)}$$

(Actual reaction rate)

The calculated reaction rate agrees remarkably well with the actual reaction rate and the agreement lends support to the correctness of the proposed reaction mechanism.

The evidence points to a chain reaction which is propagated in the gas phase and is stopped by collision at the wall of the reaction vessel. Many results of the work can be explained only by the postulation of a chain mechanism. No direct result can be cited in support of each step of the proposed mechanism, but the mechanism meets energy requirements and agrees with experimental results found in the literature. Calculations based upon the proposed reaction agree within reason with experimental results. The proposed reaction mechanism can therefore be accepted as a first step in the theoretical examination of the thermal decomposition of acetylene.

Early in this work it was thought that the decomposition reaction was propagated by thermal means instead of by a chain mechanism. In such a case much of the heat to energize the incoming acetylene must come from the refractory in spite of the large amount of heat liberated by the decomposing acetylene. In a flow process the products of the reaction tend to carry off most of the energy which they receive from the reaction. A search of the literature failed to give any data on the amount of radiat heat which the incoming acetylene

would absorb from the hot refractory wall. A method of calculating the radiant heat absorbed by a non-luminous gas and based upon the infrared adsorption spectrum of the gas was derived using a modification of the method devised by Schack and Hottel. The paper presenting the derivation of this method and the calculation of the radiant heat adsorption by acetylene is given in Appendix III. The allowable acetylene throughput, as calculated from the amount of acetylene which would be heated from room temperature to 1000° C. by radiant heat from the refractory, was insignificantly small. The theory of a thermal reaction was therefore abandoned and all new work was based upon the theory of a chain decomposition reaction.

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APPENDICES

APPENDIX I

Calculation of ΔH at 1000° C. for the decomposition of acetylene:

$$C_2H_2(g) = 2C(s) + H_2(g)$$

$$C_{p(C_2H_2)} \cdot \Delta T + \Delta H_{1000°} = (2C_{p_C} + C_{p_{H_2}}) \cdot \Delta T + \Delta H_{18°}$$

where, ΔH = heat of formation.

ΔT = temperature difference.

C_p = average molal heat capacity for the range 0° to 1000° C.

Data:

$\Delta H_{18°} = -54,800$ cal./mol.(based on graphite)

$C_{p_{C_2H_2}} = 15.1$ cal./mol.(°C.).

$C_{p_C} = 4.7$ cal./mol. (°C.).

$C_{p_{H_2}} = 7.0$ cal./mol. (°C.).

$\Delta T = 1000 - 18 = 982°$ C.

Then,

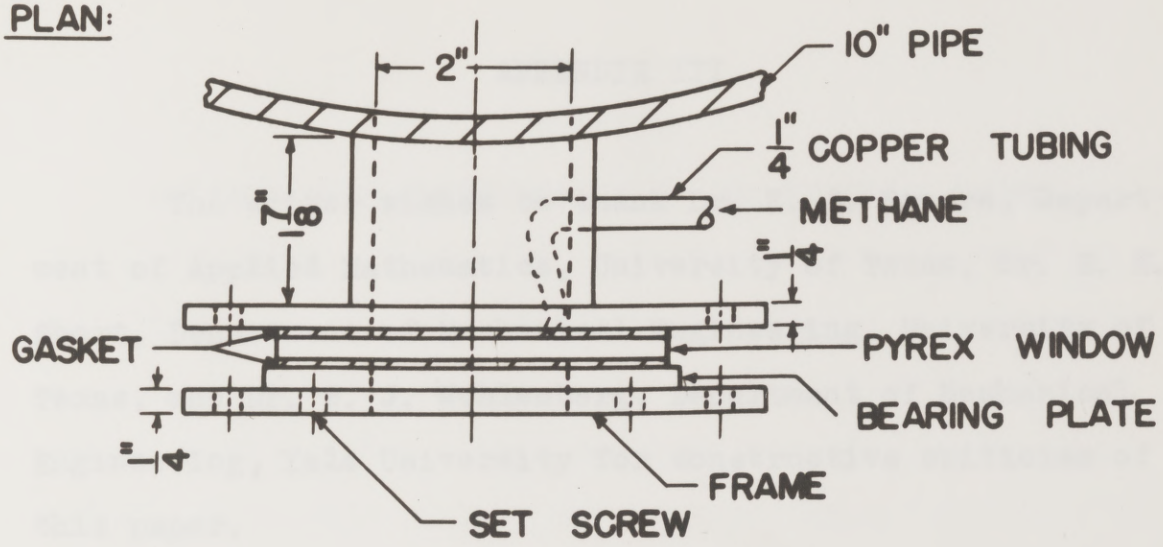
$$\Delta H_{1000°} = -54,800 + 982(9.4 + 7.0 - 15.1)$$

$$= -53,500 \text{ cal./mol.}$$

APPENDIX II

A detailed drawing of the windows used to view the carbon as it falls from the refractory is given in Figure 16. Methane is continuously blown across each Pyrex window in a direction parallel to the window to prevent carbon black from adhering to the window. In spite of the addition of methane, the passageway between the window and the 10-inch pipe fills with carbon and leaves only a small, crooked hole for viewing the falling carbon. A brass plug was fitted into the passageway and drilled with a 5/16-inch diameter hole. The velocity of the methane is great enough to prevent any carbon black from coming through the 5/16-inch diameter hole. This arrangement gives satisfactory results.

PLAN:



ELEVATION:

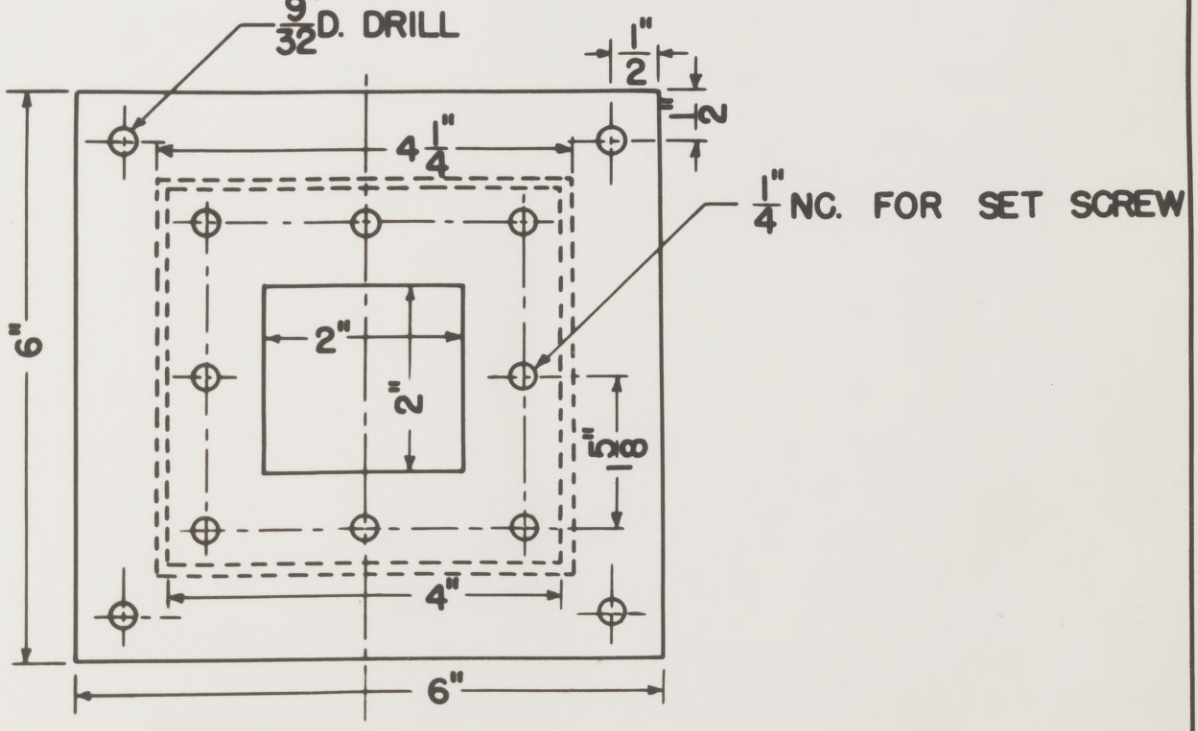


FIG. 16. WINDOWS.

APPENDIX III

The writer wishes to thank Dr. E. J. Prouse, Department of Applied Mathematics, University of Texas, Dr. B. E. Short, Department of Mechanical Engineering, University of Texas, and Dr. W. J. Wohlenberg, Department of Mechanical Engineering, Yale University for constructive criticism of this paper.

RADIANT HEAT TRANSMISSION TO NON-LUMINOUS GASES

by

E. J. Claassen

August, 1945

ABSTRACT

The infrared absorption data of a gas are used to calculate the radiant energy absorbed by the gas where the various absorption bands are treated individually and then summed to obtain the total heat transferred. A graphical solution is used to obtain the average absorption coefficient of the band. The fraction of incident radiation absorbed by the gas can then be calculated from the absorption law for various values of PL, where PL is a factor depending upon the partial pressure of the absorbing constituent in the gas, the shape of the gas mass, and the length of radiant beam through the gas. A graph giving the net radiant heat transfer between acetylene and its surrounding structure is presented.

NOMENCLATURE

A	Area of bounding surface, sq. ft.
a,b	Wave length limits of gas absorption band.
c_1	Constant in Planck's equation = 1.17×10^8 Btu/(hr)(sq. ft.)/(μ^4).
c_2	Constant in Planck's equation = 25,800 (μ)(°R.).
e	Base of natural logarithm.
I_o	Intensity of incident radiation, Btu/(hr.)(sq. ft.).
I	Intensity of transmitted radiation, Btu/(hr.)(sq. ft.).
k	Absorption coefficient, (atm.$^{-1}$)(ft.$^{-1}$).
l	Thickness of gas layer, ft.
L	Effective thickness of gas layer, ft.
P	Partial pressure of absorbing component in the gas body, atm.
q	Rate of heat transfer by radiation, Btu/hr.
q_I	Radiant heat absorbed by band I, Btu/hr.
q_s	Radiation from the surface absorbed by the gas. Evaluated at the surface temperature in Figure 9. Btu/(hr.).
q_g	Gas radiation. Evaluated at the gas temperature in Figure 9, Btu/hr.
T	Absolute temperature, °R., °F. plus 460.
$W_{B,\lambda}$	Monochromatic emissive power, Btu/(hr.)(sq.ft.)/cm.
W_B	Total emissive power for a black body, Btu/(hr.)(sq.ft.)

x Fraction of incident radiation absorbed by the gas.

ϵ_s Emissivity, dimensionless. Evaluated at surface temperature.

ϵ'_s Pseudoemissivity, $\frac{\epsilon_s + 1}{2}$

λ Wave length, microns (μ).

RADIANT HEAT TRANSMISSION TO NON-LUMINOUS GASES

Introduction

The nature of thermal radiation from gases has been known since the work of Angstrom, Julius, Paschen, and others in the early 1890's whose investigations were used in the study of molecular structure. It was not until 1924, however, that any satisfactory attempt was made to determine quantitative heat transmission from non-luminous gases. This work was done by Schack.[1] Schack was interested in radiant heat transfer from combustion gases in furnaces and his calculations, consequently, were made upon carbon dioxide and water vapor--these two gases being the main heat radiating constituents in flue gas. Schack derived a method of calculation based upon the infrared absorption spectrum of the gas. A few years later (1927) Hottel[2] made similar calculations upon carbon dioxide and water vapor using Schack's method, but obtained different results through a variance in constants. He also expanded his results to a more usable form than Schack.

In recent years careful measurements of the total radiation from water vapor, carbon dioxide, carbon monoxide,

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[1] Schack, A., "Ueber die Strahlung der Feuergase and ihre praktische Berechnung" (The Radiation of Furnace Gases and Its Practical Calculation), Z. Tech. Physik 5, 266-78, (1924).

[2] Hottel, H. C., "Heat Transmission by Radiation from Non-Luminous Gases," Trans. Am. Inst. Chem. Engr. 19, 173 (1927)

and ammonia have been made[3] and the total radiation due to sulfur dioxide has been calculated using Schack's method.[4] For other gases one must rely upon his own evaluations.

The method of calculation outlined by Schack allows a great leeway in the choice of constants. This led to a variety of results. It is the purpose of this paper (1) to outline a new method for the calculation of radiant heat transmission to non-luminous gases using infrared absorption data, and (2) present a graph for use in calculating radiant heat transmission to acetylene.

Theory

If the radiation from a black body held at constant temperature is plotted as intensity vs. wave length, the familiar curve shown in Figure 1 is obtained. This curve is continuous. A gas mass, on the other hand, will radiate in a series of bands separated by wave length regions in which there is no apparent radiation. An infinitely thick gas layer will emit radiations of black body intensity within its band limits while gas layers of lesser thickness will emit some fraction of black body radiation depending upon the gas thickness and a property of the gas designated as its absorption coefficient. The gas mass will absorb radiations within

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[3] McAdams, W. H., Heat Transmission, McGraw-Hill Book Co., Inc., New York (1942), pp. 64-72.

[4] Ibid., p. 72.

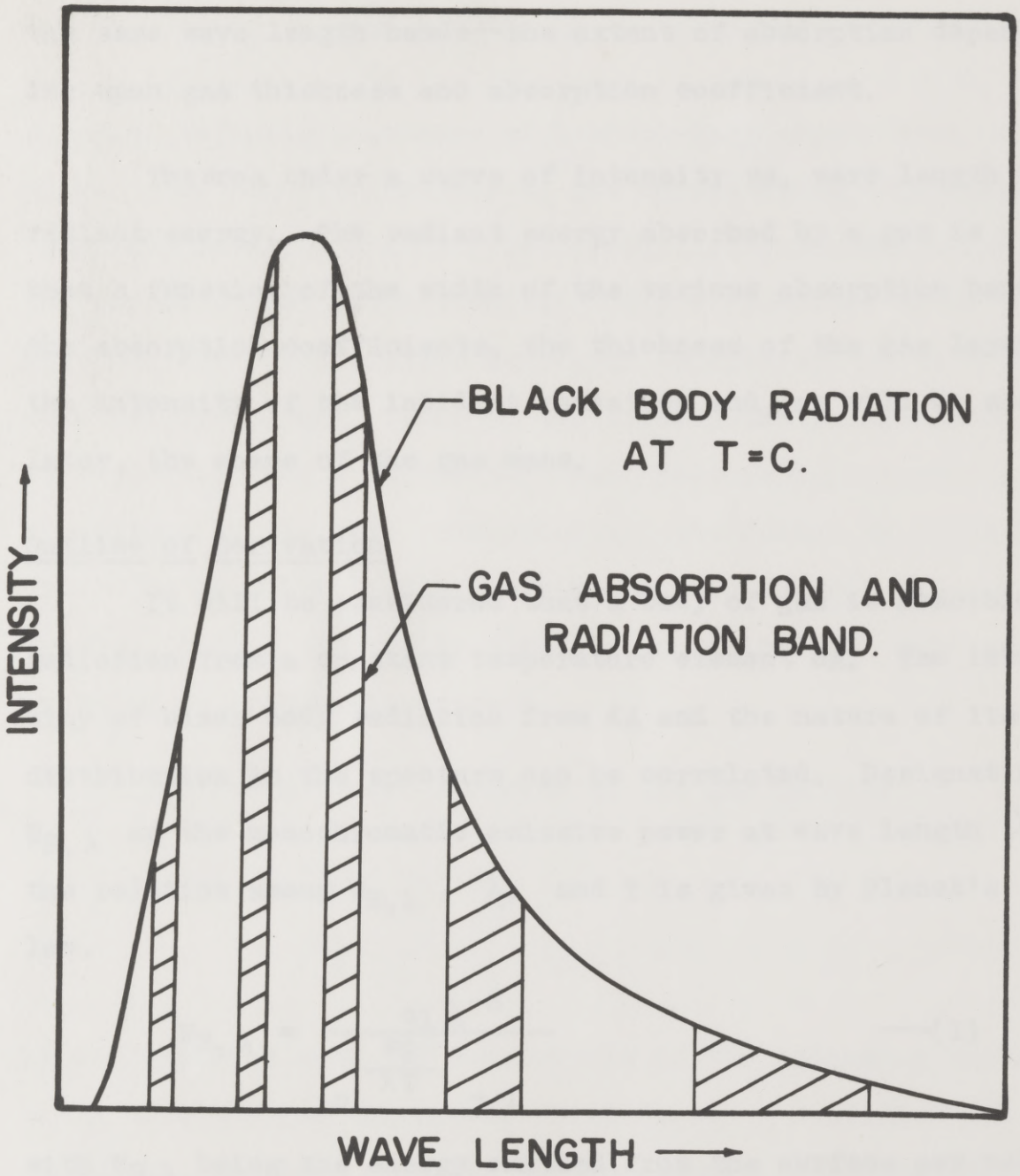

FIGURE I. COMPARISON OF RADIATION FROM A BLACK BODY AND A GAS MASS.

the same wave length bands--the extent of absorption depending upon gas thickness and absorption coefficient.

The area under a curve of intensity vs. wave length is radiant energy. The radiant energy absorbed by a gas is then a function of the width of the various absorption bands, the absorption coefficients, the thickness of the gas layer, the intensity of the incident radiation and, as will be shown later, the shape of the gas mass.

Outline of Derivation

It will be considered that a body of gas is absorbing radiation from a constant temperature element dA. The intensity of black body radiation from dA and the nature of its distribution in the specturm can be correlated. Designating $W_{B,\lambda}$ as the monochromatic emissive power at wave length λ, the relation among $W_{B,\lambda}$, λ, and T is given by Planck's law,

$$W_{B,\lambda} = \frac{c_1 \lambda^{-5}}{e^{\frac{c_2}{\lambda T}} - 1} \qquad ---(1)$$

with $W_{B,\lambda}$ being the energy emitted from the surface per unit area per unit time in the wave length interval λ to $\lambda + d\lambda$. Integrating Eq. (1) between the wave length limits of a gas absorption band gives the maximum energy available for absorption by the gas within that band.

$$W_B = \int_a^b W_{B,\lambda} \cdot d\lambda \qquad ---(2)$$

A gas of infinite thickness will completely absorb this radiation. For practical purposes, gas masses having thicknesses less than infinity and at least partially surrounded by retaining surfaces must be considered. Only a fraction, x, of the heat radiated by a surface having an emissivity, ϵ_s, will be absorbed by the gas. Some of the transmitted radiation will be reflected from a surface and have further opportunity for absorption by the gas. Consequently, the factor by which Eq. (2) is to be multiplied is a pseudoemissivity, ϵ'_s, lying between ϵ_s and 1. A usually adequate approximation[5] consists in using an arithmetic average.

The radiant heat absorbed by the gas is thus

$$q/A = \epsilon'_s \cdot x \cdot W_B$$

$$= \epsilon'_s \cdot x \cdot \int_a^b W_{B,\lambda} \cdot d\lambda \qquad ---(3)$$

W_B is dependent upon the temperature of the radiating surface and x upon the gas thickness. With W_B and x evaluated for each band, the heat absorbed by the gas can be calculated.

The extent of radiant heat absorption varies with wave length. It is determined by the absorption law

$$\frac{I}{I_o} = e^{-kl} \qquad ---(4)$$

---

[5] Ibid., p. 68.

If the gas under consideration is not pure, the concentration of the component under consideration must be considered. Hence, the above equation may be rewritten as

$$\frac{I}{I_o} = e^{-kPl} \qquad ---(5)$$

Eq. (5) gives the fraction of incident radiation transmitted by a gas having an absorption coefficient k, partial pressure of absorbing constituent P, and gas thickness l. The equation can be used to show the fraction of initial radiation absorbed. Since it is assumed that no radiation is reflected from a gas mass, it follows that

$$\frac{I_o - I}{I_o} = 1 - e^{-kPl} \qquad ---(6)$$

where,

$$\frac{I_o - I}{I_o} = x = \text{fraction of incident radiation absorbed.}$$

Absorption coefficients will be considered as constant with temperature since this is necessary to be able to use coefficients determined at room temperature. Absorption is known to increase slightly with temperature, thus giving calculated values of heat transfer which are on the low side at high temperatures.

Infrared absorption data are usually plotted as per cent of initial radiation transmitted (or absorbed) vs. wave-

length. It can be transposed to a plot of intensity vs. wave-length and such a plot is shown in Figure 2. The area under the dotted curve corresponds to the heat absorbed by that band of gas for a certain Pl value and radiating surface temperature. Since the absorption coefficient, k, is assumed constant for each wave-length, it must also have a constant average value for the entire band. With k constant, the ratio of the heat absorbed by the gas to that emitted by the black body is constant for any value of Pl regardless of the temperature. In other words, absorption is independent of the intensity of incident radiation. This ratio of heat absorbed to heat emitted may be represented on the graph by a ratio of areas and corresponds to the left side of Eq. (6), as shown in Eq. (6a).

$$\frac{I_o - I}{I_o} = 1 - e^{-kPl}$$

$$\frac{(I_o - I)_{av.} \cdot \Delta\lambda}{(I_o)_{av.} \cdot \Delta\lambda} = 1 - e^{-k_{av.}Pl}$$

$$\frac{\text{Area under absorption curve}}{\text{Area under black body curve}} = 1 - e^{-k_{av.}Pl} \quad ---(6a)$$

Substitution into Eq. (6a) will lead to a value of k for the band. The value of Pl used in this substitution must correspond to the condition of the gas when the infrared absorption data were obtained.

If the incident radiation is considered to be that of a black body (which can be calculated from Planck's equation and corrected with the emissivity), the only unknown remaining

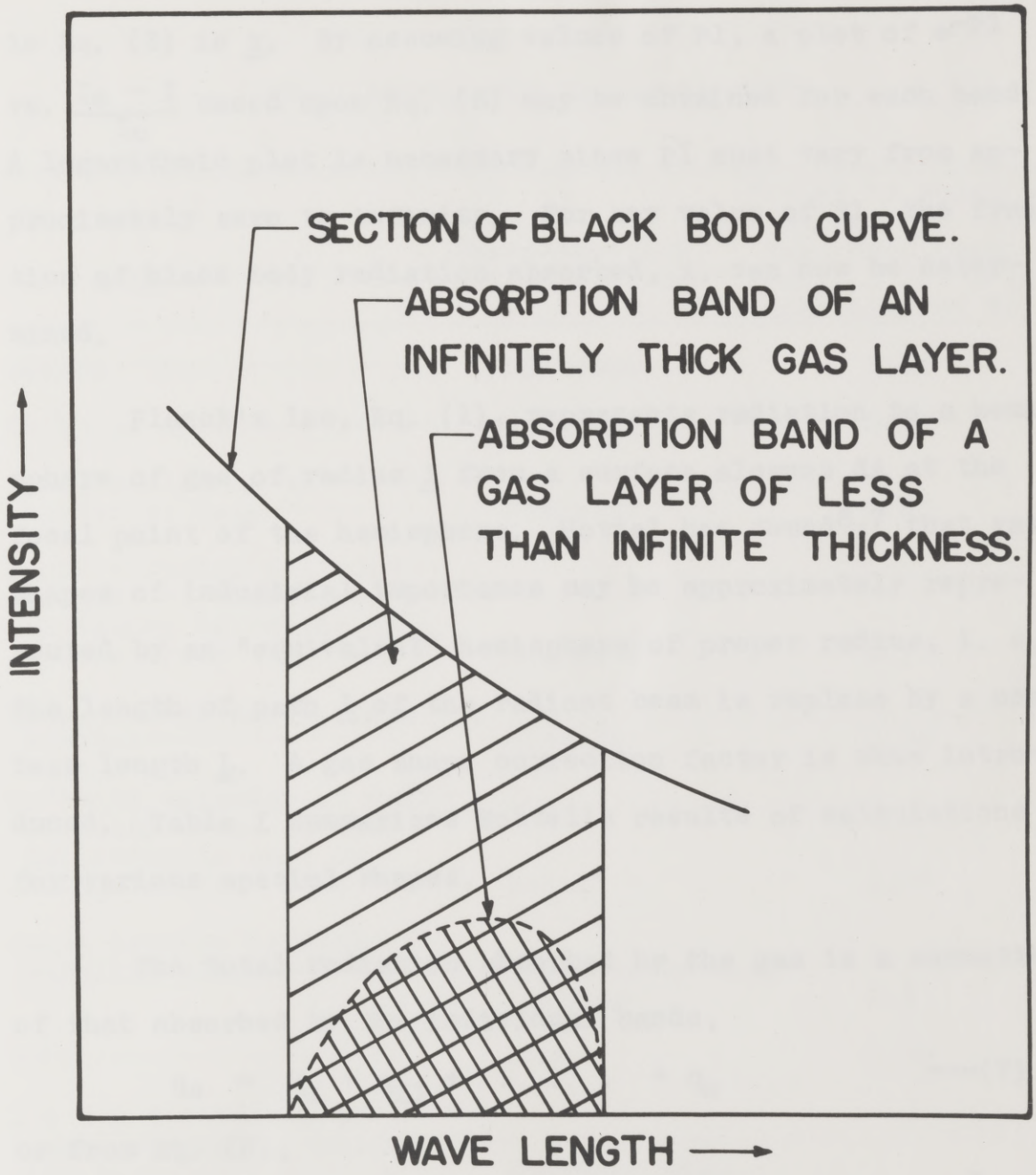

FIGURE 2. INFLUENCE OF GAS THICKNESS UPON ABSORPTION.

in Eq. (3) is x. By assuming values of Pl, a plot of e^{-Pl} vs. $\frac{I_o - I}{I_o}$ based upon Eq. (6) may be obtained for each band. A logarithmic plot is necessary since Pl must vary from approximately zero to infinity. For any value of Pl, the fraction of black body radiation absorbed, x, can now be determined.

Planck's law, Eq. (1), represents radiation to a hemisphere of gas of radius l from a surface element dA at the focal point of the hemisphere. Hottel has found[6,7] that gas shapes of industrial importance may be approximately represented by an "equivalent" hemisphere of proper radius, i. e., the length of path l of the radiant beam is replace by a mean beam length L. A gas shape correction factor is thus introduced. Table I summarizes Hottel's results of calculations for various special shapes.

The total radiation absorbed by the gas is a summation of that absorbed by the individual bands,

$$q_s = q_I + q_{II} + \ . \ . \ . \ + q_n \qquad ---(7)$$

or from Eq. (3),

$$q_s/A = \epsilon'_s \left[(xW_B)_I + (xW_B)_{II} + \ . \ . \ . \ + (xW_B)_n \right] \qquad ---(8)$$

The total heat retained by the gas is the difference between

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[6] Ibid., pp. 68-9.

[7] Hottel, loc. cit.

TABLE I

BEAM LENGTHS FOR GAS RADIATION[6]

Shape	Characterizing dimension, D	Factor by which D is multiplied to obtain mean beam length L for average value of PL
Sphere	Diameter	0.60
Infinite cylinder	Diameter	0.90
Same, radiating to center of base	Diameter	0.90
Right circular cylinder height = diameter, radiating to center of base	Diameter	0.77
Same, radiating to whole surface	Diameter	0.60
Infinite cylinder of half-circular cross section. Radiating to spot on middle of flat side	Radius	1.26
Space between infinite parallel planes	Distance between planes	1.8
Cube	Edge	0.60
1 x 2 x 6 rectangular parallelepiped, radiating to	Shortest edge	
2 x 6 face	----------	
1 x 6 face	----------	
1 x 2 face	----------	1.06
All faces	----------	

[6] McAdams, W. H., op. cit., pp. 68-9.

that absorbed and that reradiated to the surface:

$$q/A = \left[\epsilon'_s q_s + (1 - \epsilon'_s) q_g - q_g\right] = \epsilon'_s (q_s - q_g) \qquad ---(9)$$

where q_s represents the radiation from the surface absorbed by the gas and q_g the heat radiated by the gas.

Radiant Heat Absorption by Acetylene

Acetylene has five absorption bands in the infrared region. The range of these bands is given in Table II.

TABLE II

ABSORPTION BANDS OF ACETYLENE

Band	Limits, μ	Width, μ
I	2.1 - 2.75	0.65
II	2.8 - 3.3	0.5
III	3.6 - 4.0	0.4
IV	7.0 - 8.3	1.3
V	12.0 - 15.7	3.7

The work of Burmeister[8] was used to obtain the above values. It was necessary to use data for which the partial pressure of the gas and the thickness of the sample were given. These

[8] Burmeister, "Untersuchungen uber die ultraroten Absorptionspektra einiger Gase." Berichte der Deutschen Physical Gesellschaft, 1913, p. 604.

limitations eliminated the work of several investigators. The conditions under which Burmeister made his investigation are given in Table III.

TABLE III

INFRARED ABSORPTION INVESTIGATION CONDITIONS

Band	Tube Length, (L)	Pressure, (P)	PL
I	0.656 ft. (20 cm)	1 atm.	0.656
II	"	"	"
III	"	"	"
IV	"	0.1318 atm. (100 mm)	0.0865
V	"	"	"

Plots of intensity vs. wave length for the five absorption bands as transposed from graphs of per cent absorption vs. wave length are given in Figures 3 to 7. Corresponding sections of the black body radiation curve are included and are considered to be straight lines between band limits. Areas are determined under both the black body and the absorption curves. Substitution of these areas into Eq. (6a) allows the calculation of the absorption coefficient, k_{av}, for each band. With $k_{av.}$ evaluated, Eq. (6) is used to calculate the

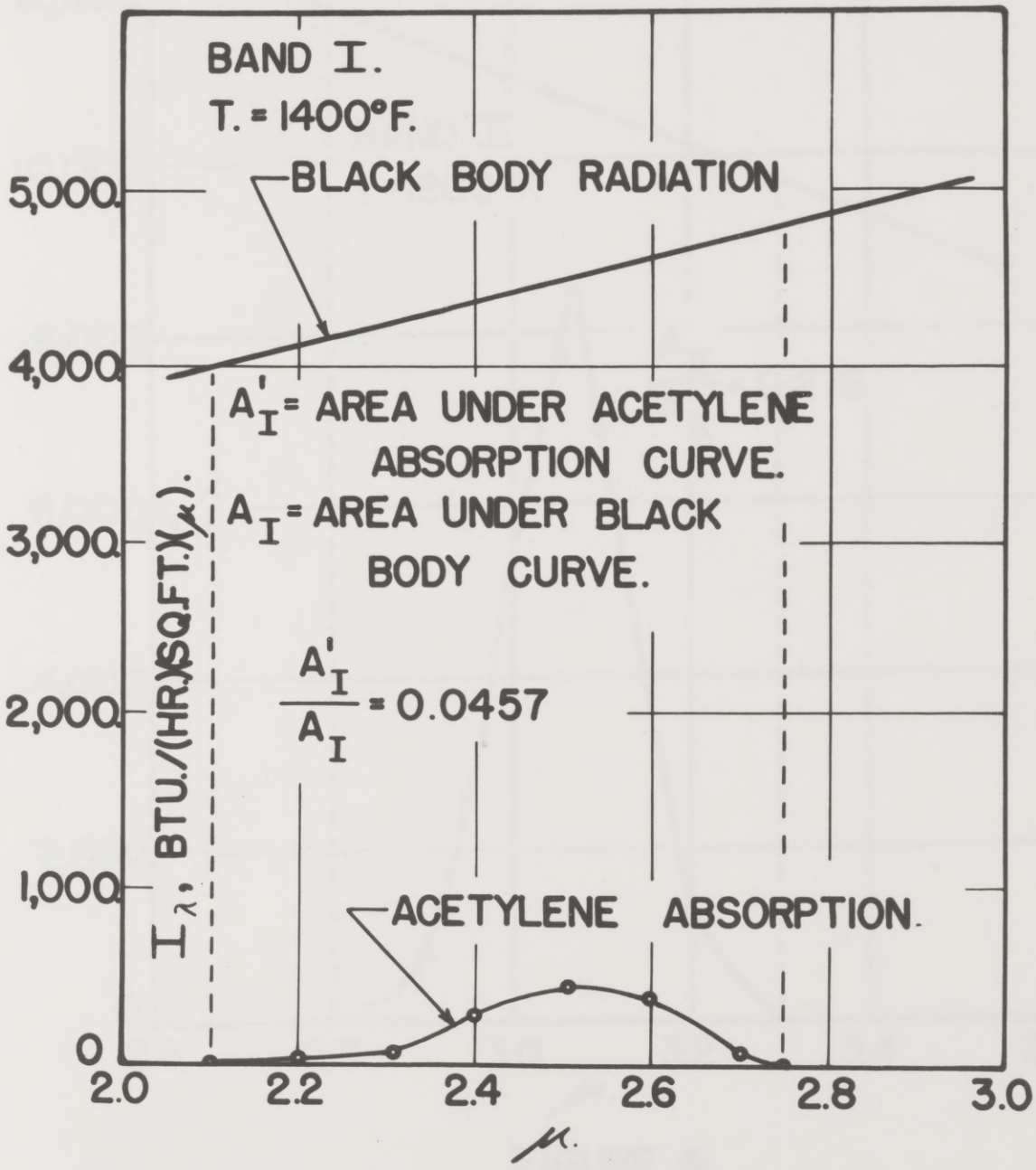


FIGURE 3. ABSORPTION OF BLACK BODY RADIATION BY ACETYLENE BAND I.

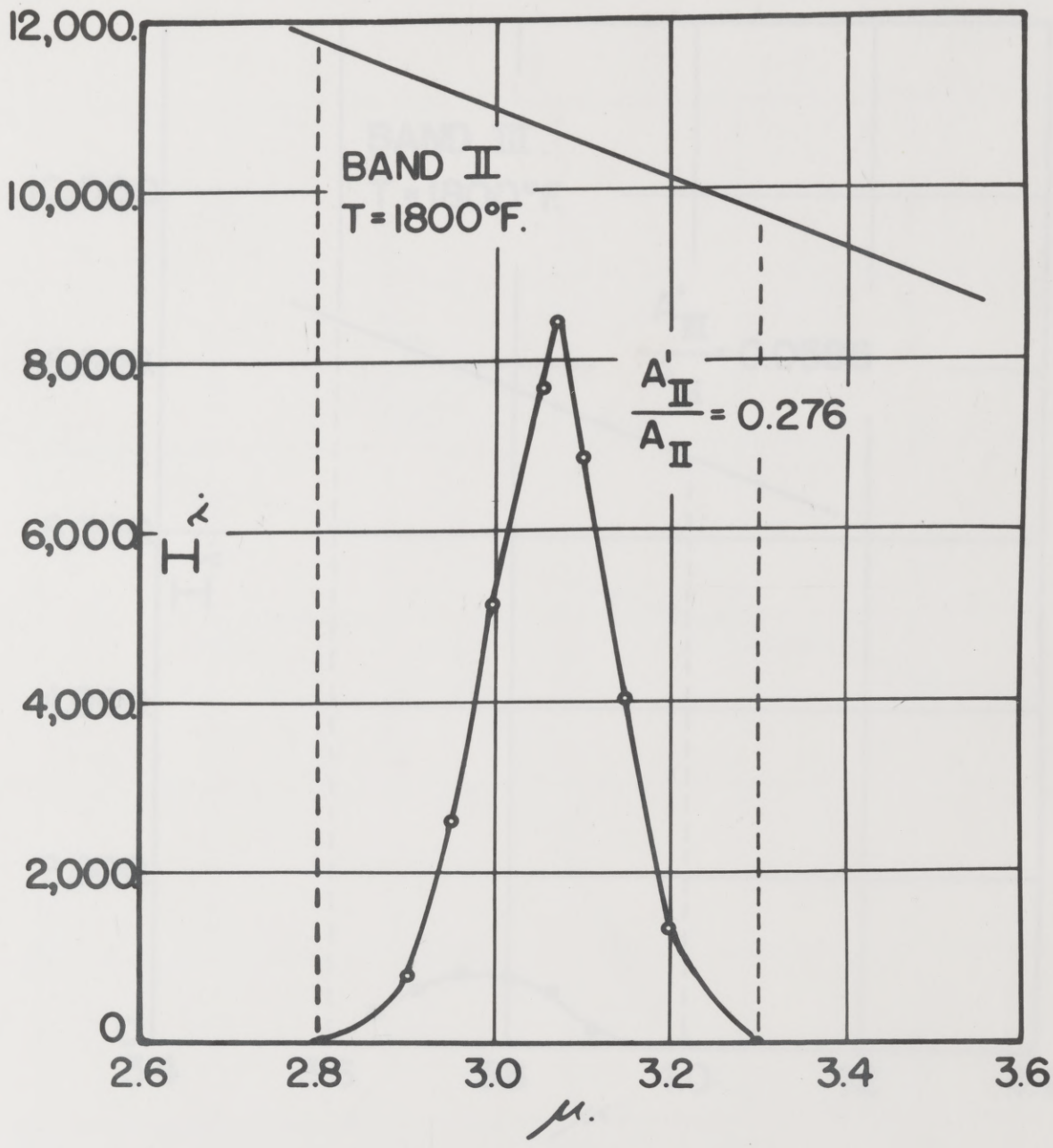

12,000.
10,000.
8,000.
6,000.
4,000.
2,000.
0
BAND II
T = 1800°F.
$\frac{A'_{II}}{A_{II}} = 0.276$
H_λ
2.6
2.8
3.0
3.2
3.4
3.6
μ.

FIGURE 4.

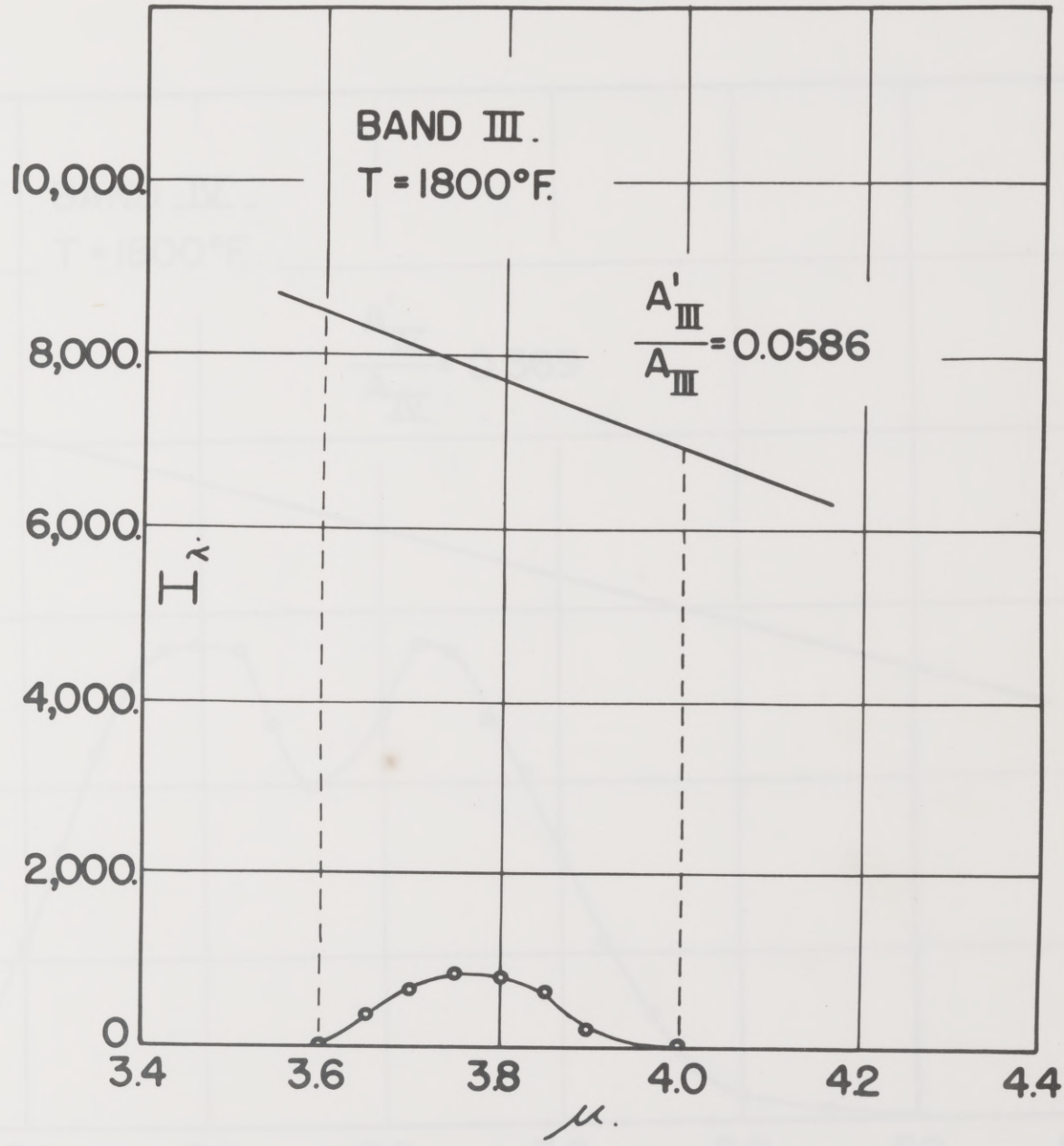

BAND III.
T = 1800°F.
$\frac{A'_{III}}{A_{III}} = 0.0586$
10,000.
8,000.
6,000.
4,000.
2,000.
0
H_λ
3.4
3.6
3.8
4.0
4.2
4.4
μ.

FIGURE 5.

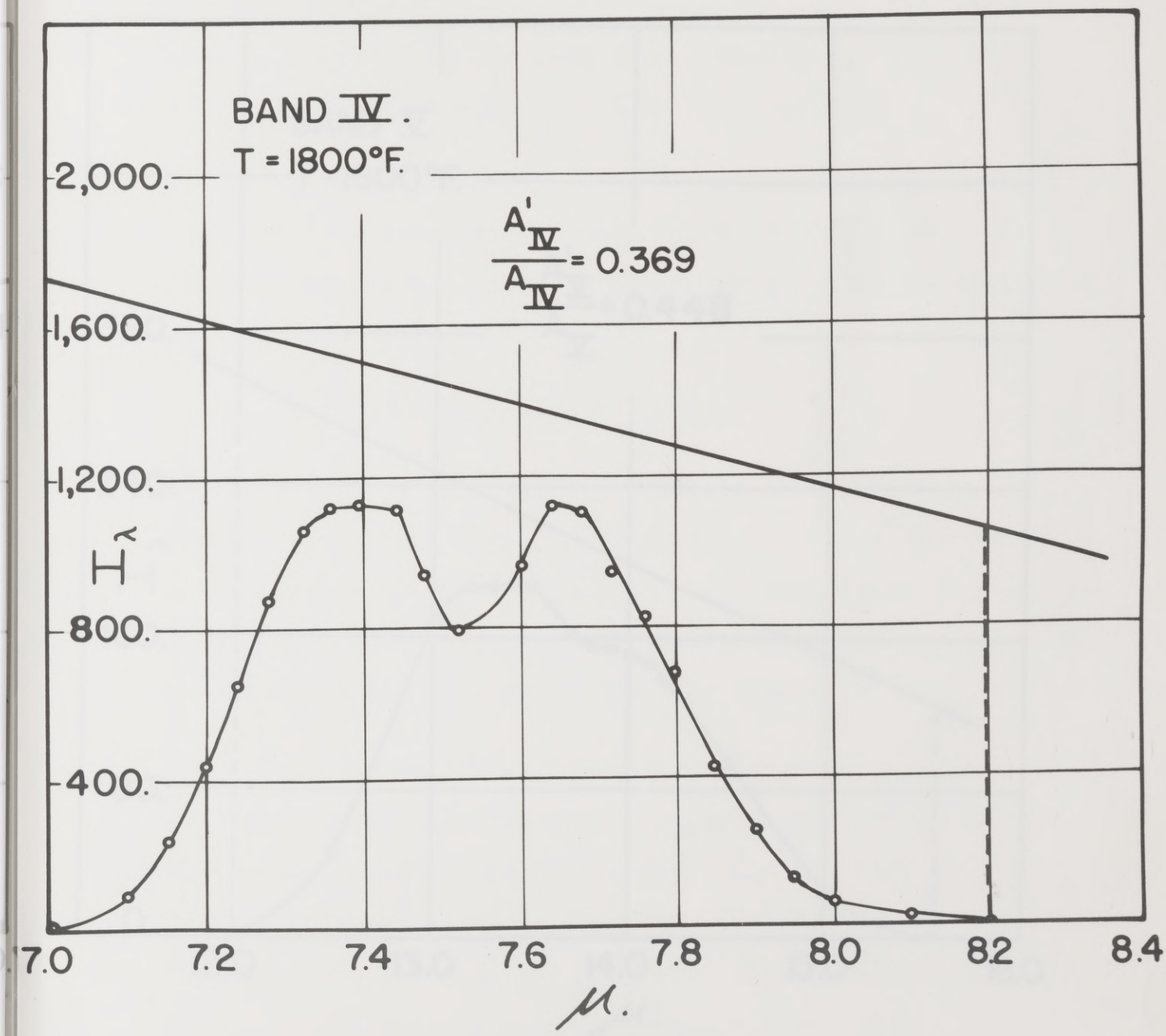

BAND IV.
T = 1800°F.
2,000.
1,600.
1,200.
800.
400.
$\frac{A'_{IV}}{A_{IV}} = 0.369$
H_λ
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
μ.

FIGURE 6.

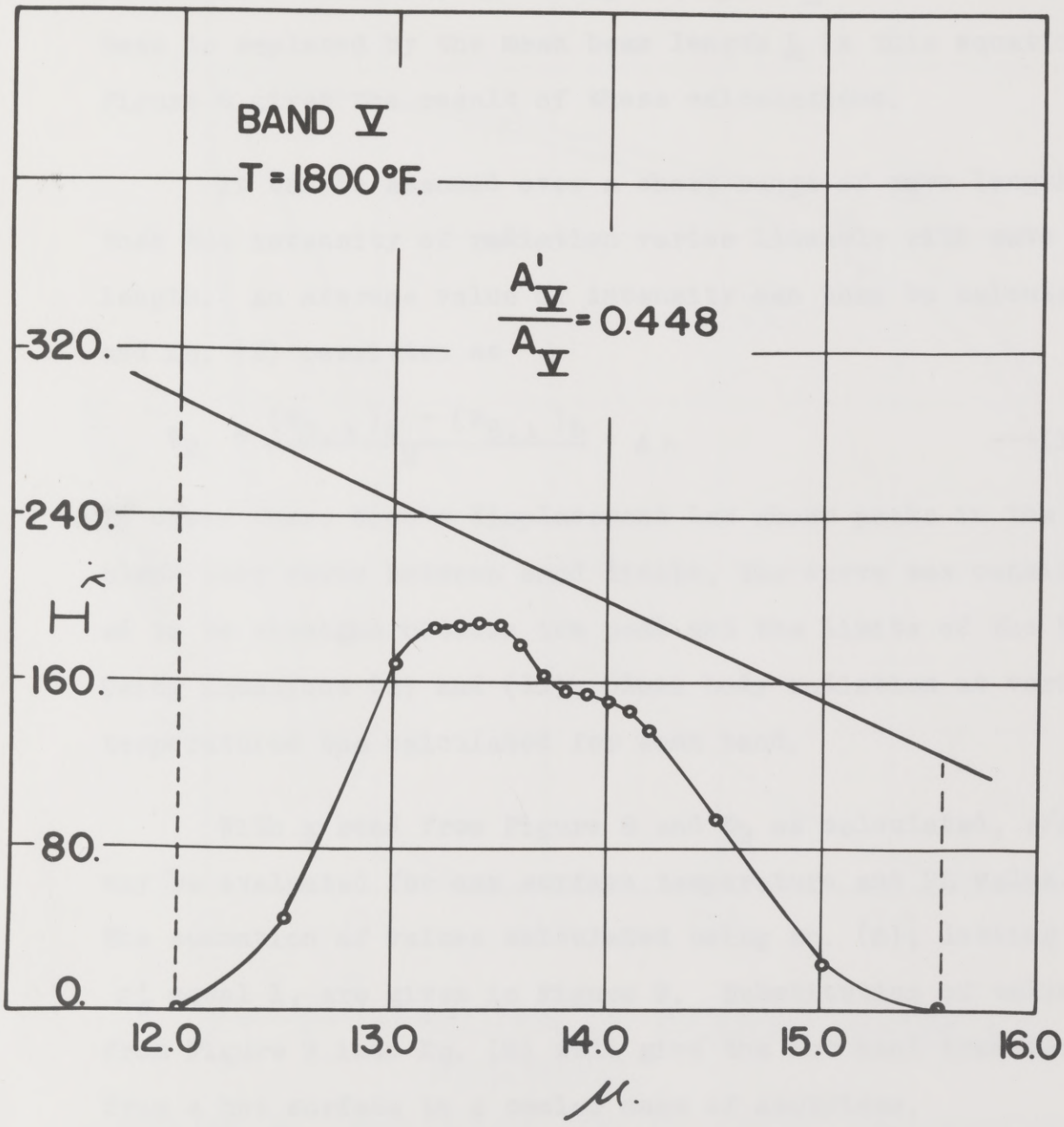

BAND V
T = 1800°F.
$\frac{A'_V}{A_V} = 0.448$
320.
240.
160.
80.
0.
H_λ
12.0
13.0
14.0
15.0
16.0
μ.

FIGURE 7.

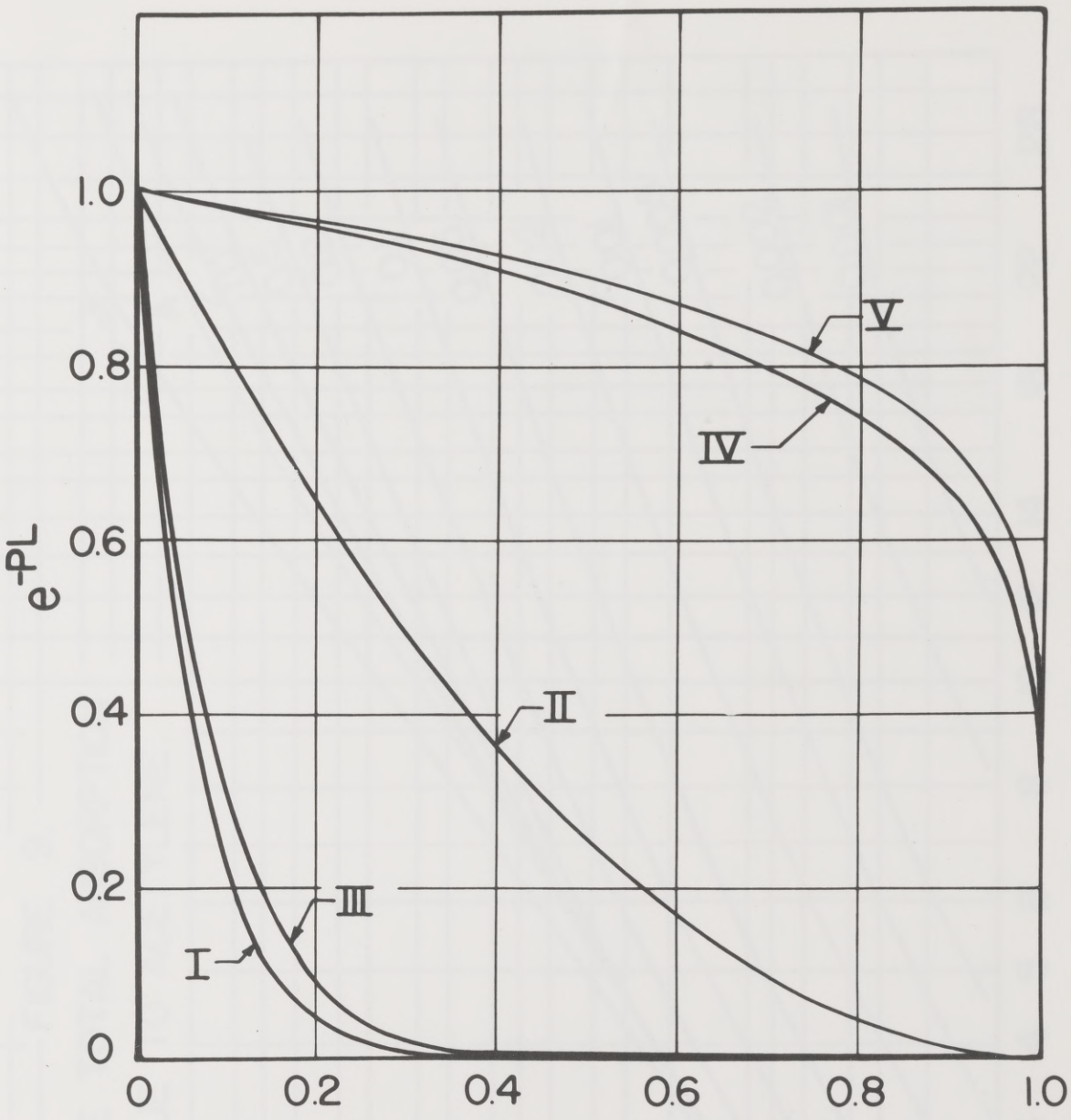
fraction of incident radiation, x, absorbed by each band for various values of PL. The length of path l of the radiant beam is replaced by the mean beam length L in this equation. Figure 8 gives the result of these calculations.

It can be assumed over a short range of wave length that the intensity of radiation varies linearly with wave length. An average value of intensity can then be calculated and Eq. (2) rewritten as

$$W_B = \frac{(W_{B,\lambda})_a - (W_{B,\lambda})_b}{2} \cdot \Delta\lambda \qquad \text{---(10)}$$

In cases where Wien's displacement law shows peaks in the black body curve between band limits, the curve was considered to be straight between the peak and the limits of the band. Using Equations (1) and (10), black body radiation at various temperatures was calculated for each band.

With x read from Figure 8 and W_B as calculated, q/A may be evaluated for any surface temperature and PL value. The summation of values calculated using Eq. (8), letting ϵ'_s equal 1, are given in Figure 9. Substitution of values from Figure 9 into Eq. (9) will give the net heat transfer from a hot surface to a cooler mass of acetylene.



$$X = \frac{I_o - I}{I} = \text{FRACTION OF INCIDENT RADIATION ABSORBED.}$$

FIGURE 8. INFLUENCE OF PL UPON ABSORPTION OF RADIATION BY ACETYLENE.

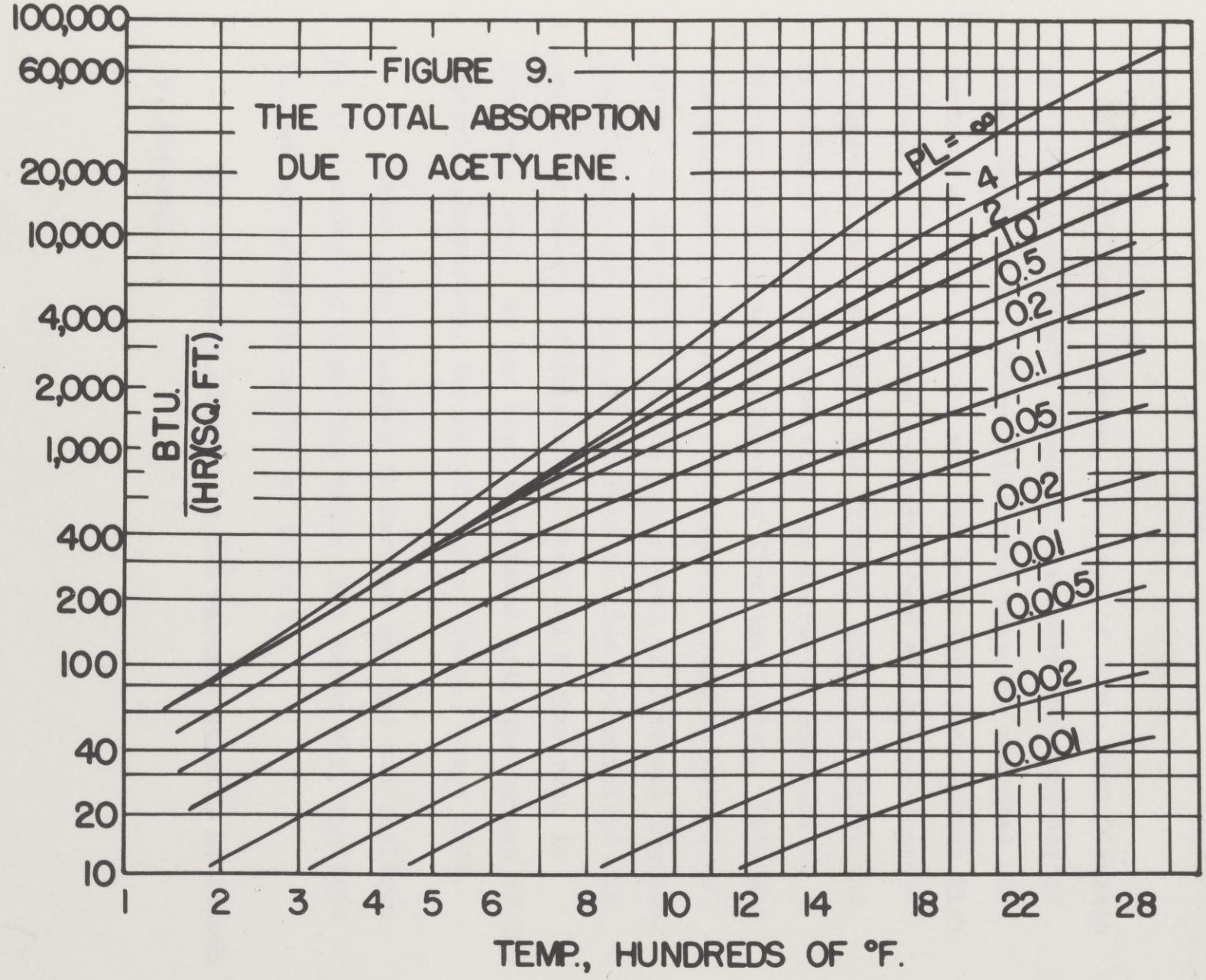


FIGURE 9.
THE TOTAL ABSORPTION
DUE TO ACETYLENE.
BTU. / (HR)(SQ. FT.)
100,000
60,000
20,000
10,000
4,000
2,000
1,000
400
200
100
40
20
10
PL = ∞
4
2
1.0
0.5
0.2
0.1
0.05
0.02
0.01
0.005
0.002
0.001
1
2
3
4
5
6
8
10
12
14
18
22
28
TEMP., HUNDREDS OF °F.

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